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MULTICOLOR ELECTROCHROMIC DISPLAYS
EXPLORATORY DEVELOPMENT

FINAL REPORT FOR THE PERIOD
August 1, 1985 through March 31, 1988

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Multicolor electrochromic cells using a rare-earth diphthalocyanine as the switchable material offer advantages over other flat-panel technologies for several types of information displays. This exploratory development effort addressed the issues of cycle life, red-color improvement, and counter-electrode performance.

Major increases in the orange/green or orange/blue-green cycle life of lutetium diphthalocyanine electrodes in aqueous chloride electrolytes were achieved, respectively, by the use of a Nafion binder on the dye film and by incorporation of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) in the liquid electrolyte. Three failure modes were identified from changes in the switching charge and absorption spectra that occurred during long-term voltage-pulse cycling. Lifetimes greater than 3×10^6 cycles for the orange/blue-green transition were attained with AMPS additives, and

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electrode failure was then due to contact corrosion rather than deterioration of the electrochromic system. Orange/blue cycling was investigated less extensively; further research is needed to extend the life in this mode beyond 5×10^4 cycles. Improvement of the red color by using neodymium diphthalocyanine instead of the lutetium compound was shown to be feasible.

Reliable performance of the silver-silver chloride counter electrode in a chloride electrolyte was verified by controlled-current cycling that simulated the counter-electrode response in a display cell. Lead-lead fluoride was shown in the same way to be a suitable alternative, usable in chloride-free electrolytes containing the more inert fluoride anion. It was concluded from the experimental results that further development of diphthalocyanine electrochromics can lead to practical displays. Specific research and development tasks are recommended.

The report also includes an assessment of the multicolor electrochromic system in relation to four other flat-panel technologies for military aircraft and large-screen displays. In comparison with liquid crystals, the electrochromic has the inherent advantages of open-circuit memory, higher resolution due to coincident color, wider viewing angle, noncritical cell thickness, and fast response at low temperatures. In a full video mode, the electrochromic would require higher power than liquid crystals, but in a graphic or message display that is infrequently changed, the electrochromic would have a power advantage because of its open-circuit memory.

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I. INTRODUCTION

Several years ago, Rockwell International originated the concept of a multicolor flat-panel display technology based on electrochromic rare-earth diphthalocyanine dye compounds. The first detailed experimental evaluation was made under a contract with the Naval Air Development Center.[1,2] Technical feasibility of such displays was confirmed in subsequent developmental efforts for the Office of Naval Research[3,4] and in basic research projects sponsored coordinatively by that office* and the Air Force Office of Scientific Research.**

This new display medium offers a unique combination of attractive features that are desired in electronic displays for Naval aircraft, large-screen displays, and other applications. Among its capabilities are: Many colors generated in a single display material (coincident color), simple thin cell structure, light weight, sunlight readability, very low input voltage and power, open-circuit memory, wide operating temperature range, and a prospect of resistance to nuclear radiation.

The present exploratory development program was designed to improve the electrochromic device performance, generate a plan for matrix addressing, and provide a technology base for advanced development. The experimental effort was focused primarily on extension of the cycle life and improvement of the red display color. Most of the work was done with lutetium diphthalocyanine as the electrochromic material, but neodymium diphthalocyanine was used in the color experiments. The cycling characteristics of two counter electrode systems, Ag/AgCl and Pb/PbF_2, were evaluated briefly.

The diphthalocyanines are sandwich compounds, which may be represented in a chemically reduced state by the structural formula I where M denotes the rare-earth element.

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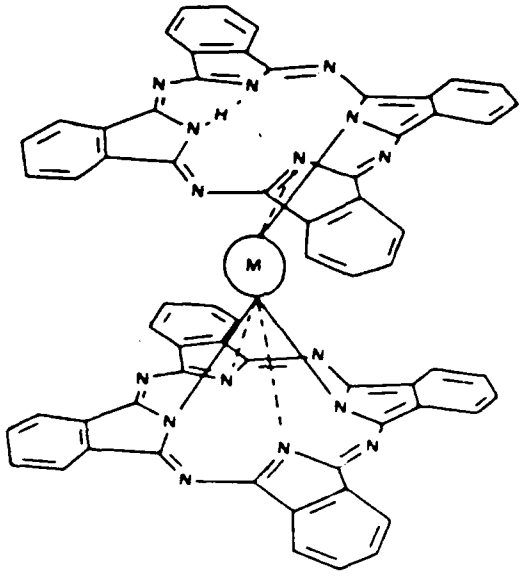


I

The large organic ring is usually abbreviated Pc, and (I) as $MHPc_2$.

All of the electrolytes in the display-electrode studies contained chloride ion. Approaches that were evaluated for extending the cycle life of the dye film included variation of the transparent conductive substrate and the pH of the electrolyte, incorporation of several types of organic additives directly in the dye film or in the electrolyte, and treatment of the electrode with a surfactant or a silanizing agent.

This report presents the results of these laboratory investigations and discusses the multicolor electrochromic and other flat-panel display technologies in relation to aircraft and large-screen display requirements. Matrix-drive information developed under this contract is documented elsewhere. Experimental matrix-drive development and the construction of advanced display models are reserved for the future.

II. EXPERIMENTAL PROCEDURES

This section describes the materials used in the investigation, the cells and electrodes, instrumentation, and measurement procedures.

A. MATERIALS

1. Rare-Earth Diphthalocyanines

Lutetium diphthalocyanine was prepared by the method of Moskalev and Kirin,[5] as described in an earlier report.[1] In this procedure, the rare-earth acetate is heated with o-phthalonitrile to 300°C to bring about the dye-ring formation. The resulting solid product is ground to a fine powder, washed successively with acetic anhydride, acetone, and dimethylformamide, and dried in air. The final purification occurred in the course of vacuum sublimation to form the electrode films.

Neodymium diphthalocyanine was formed in the same manner by reaction between the acetate and the nitrile. Because the neodymium compound tends to decompose on sublimation, it was isolated from the reaction product by the electrolytic method of Moskalev, Shapkin, and Darovskikh.[6] The crude dye product was dissolved in dimethylformamide containing about 1 vol % hydrazine hydrate. Pure crystalline $NdPc_2$, in the green state, was recovered from this solution by anodic deposition at a gold electrode. A solution spectrum of this solid dissolved in benzene and an IR spectrum of the solid itself matched those reported by Moskalev et al.[6]

2. Special Chemicals

Preliminary experiments with Nafion (a DuPont perfluorosulfonic acid polymer) as a binder for the dye film were performed with a 1% Nafion solution in an aliphatic alcohol-water solvent, obtained from Research Organic/Inorganic Chemical Corp. In subsequent detailed work with this binder, a 5 % Nafion solution from Aldrich Chemical Co. was used. The acid form of the 2-acrylamido-2-methylpropanesulfonic acid (AMPS) additive was Lubrizol 2401; the sodium-salt form was Lubrizol 2403A. Surfactants, which were investigated briefly as pre-treating agents for the dye film, were Witcamine AL42-12 (an imidazoline preparation) and Dow 193 Surfactant (a

silicone-polyoxyalkylene copolymer). Silanization of the tin oxide substrate was explored using Dynasylan IMEO (an imidazoline silane) and Dow Z6020, which contains N-(2-aminoethyl)-3-aminopropyltrimethyl silane.

The AMPS polymer was prepared by treating 200 g of an air-free 50 wt % solution of AMPS monomer in distilled water with 0.01g $FeSO_4 \cdot 7H_2O$ and 0.25 g of 0.5 % H_2O_2. At 70°C, the mixture gelled in approximately 1 min. It was then vacuum-dried at room temperature and ground to a powder.

Propylene glycol and two poly(ethylene glycol) (PEG) preparations with average molecular weights of 300 and 3350 were from J.T. Baker Chemical Co.

3. Conductive Substrates

Most of the dye electrodes were prepared on pyrolytic tin oxide from Corning Glass Works, which had a sheet resistivity of 7-10 or 21-24 ohms/square. Effects of varying the substrate were investigated with a commercial sputtered indium-tin oxide (ITO)/glass (~ 65 ohms/square) and a proprietary ITO/polyester material (~ 34 ohms/square) from another commercial supplier.

4. Contact and Sealant Materials

Electrical contact to the dye plate was made with DuPont 4929 conductive silver paste, which was cured at room temperature. At the beginning of the program, the contact was isolated from the electrolyte with Apiezon W-100, a black laboratory wax that is applied in the molten state. For the long-term cycling experiments, the contact was sealed instead with a water-resistant epoxy resin, Epotek ALT5-TO, from Epoxy Technology. This is a thixotropic version of Epotek 302-3. The epoxy was cured at room temperature to minimize effects on the dye film.

B. PREPARATION OF ELECTRODES

1. Display Electrodes

Tin oxide/glass or ITO/glass substrates 1.27 × 5 cm were cleaned by overnight exposure to isopropyl alcohol in a Soxhlet extractor. This was followed by a 15-min soak in a water solution of Alconox or Pierce RBS 35 detergent. The substrates were then

thoroughly rinsed, air-dried, and assembled in a glass holder for insertion in the vacuum chamber.

The ITO/polyester substrates were prepared by a different procedure. Strips 1.27 cm wide were first reinforced in the upper half by attaching a piece of microscope-slide glass to the nonconductive side with Super Glue, a cyanoacrylate adhesive. After the glue hardened, the electrodes were rinsed in isopropyl alcohol and air-dried.

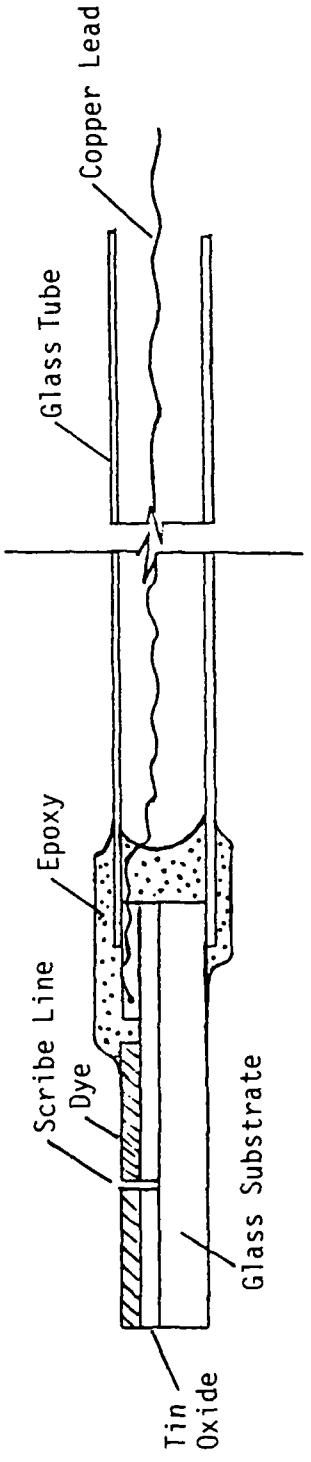
Lutetium diphthalocyanine films were vacuum-deposited by thermal sublimation at approximately 3×10^{-6} torr.[1] To improve adhesion of the dye, the glass substrates were heated with an infrared lamp during the deposition.[1] A set of eight electrodes with uniform equivalent dye thickness could be prepared in a single deposition run by maintaining the source-to-substrate distance at about 15 cm.

The neodymium diphthalocyanine electrodes were prepared on tin oxide/glass by a spraying technique. A concentrated benzene solution of the anodically formed diphthalocyanine was sprayed onto a warmed tin oxide substrate by means of a small artist's spray brush. After the desired thickness was obtained, as indicated by color depth and uniformity, the coated substrate was annealed by further heating on a hot plate for 10 to 15 min.

Details of the display-electrode construction are shown in Figure 1. The glass tube surrounding the copper lead was slotted at the lower end to maintain its alignment with the plate while the epoxy was curing. The switchable area, which was measured for each electrode, was approximately 2 cm^2. The lower portion of the dye film was separated from that area by a scribe line extending through the tin oxide. This unswitchable area was later positioned inside the guide slot of a plastic holder in the original cell design.[4] It was also useful to show color contrast.

2. Counter and Reference Electrodes

The electrolytes in all of the display-electrode cycling experiments contained chloride ion, usually as 1M KCl. To ensure good electrochemical reversibility and minimum polarization in this type of medium, the counter electrodes were silver-silver chloride (Ag/AgCl), with a coulombic capacity far greater than that of the dye electrodes. Strips of silver foil 0.5 × 3.0 cm were coated with a silver oxide-water paste, which was thermally converted to porous silver by heating to 400°C. Each electrode was



Film Thicknesses Not to Scale

Figure 1. Display Electrode Structure

then anodized at 3 mA/cm^2 in 1M KCl to convert a portion of the porous silver to silver chloride. After it was cycled several times, the electrode was removed at roughly the 50 % state-of-charge, which corresponded to ~ 1.5 C/cm^2 of counter electrode capacity, based on the geometric, or projected, area. This is three orders of magnitude greater than the charge density of the display electrode.

Reference electrodes for use in the chloride electrolytes were prepared in the same way, but since they were not required to carry appreciable currents, they were of smaller areas, formed on silver wires of 0.1 or 0.2 cm diameter and 5 cm length.

Lead/lead fluoride (Pb/PbF_2) electrodes were tested for future use in electrolytes containing fluoride instead of chloride ion. These electrodes were formed by anodizing freshly abraded lead foil in 1M KF at 1 or 2 mA/cm^2. The presence of a fluoride coating was confirmed by x-ray powder diffraction patterns.

C. INCORPORATION OF ORGANIC ADDITIVES

Several organic additives were investigated as means for improving the display-electrode performance. Some were incorporated in the electrode before the cell was assembled. Others were added to the electrolyte solution so that they could interact in situ with the dye film. Details on introduction of the additives are given below. The structural formulas of these materials are shown in context with the discussion of their effects in Section III.

1. Nafion

Initially, the vacuum deposited dye film was simply dipped in the 1% Nafion solution and allowed to dry. In other instances, a thicker Nafion coating was applied by allowing several drops of the solution, retained by an O-ring, to evaporate on top of the dye surface. For other variations of this process, the film was pretreated with a surfactant solution (Part 2 below) to open its structure prior to the Nafion exposure or preoxidized to the orange state by reaction with gaseous chlorine.

In the course of this project, an improved method for depositing Nafion films, developed by C. R. Martin and co-workers, became available.[7] Nafion-treated electrodes for the long-term cycling experiments were prepared by the Martin procedure, as follows: The 5 % alcoholic Nafion solution was neutralized with sodium hydroxide to

form the Nafion sodium salt. An equal volume of ethylene glycol was then added and several drops of the mixture were placed on the dye-coated electrode surface. The low-boiling alcohol and water components were evaporated at ~ 80°C, and the higher-boiling glycol was then removed by evaporation at ~ 120°C. This procedure results in a transparent Nafion coating with properties similar to those of the original polymer.[7] During the solvent evaporation, the lutetium diphthalocyanine color changed from green to orange, indicating the presence of an unidentified oxidizing agent. However, the treated film was readily converted to the green state electrochemically and could be cycled many times.

2. Surfactants

A surfactant treating method was adapted from that described previously for opening the structure of lutetium diphthalocyanine films on nonconductive substrates.[8] Separate solutions of Dow 193 (49 g in 40 ml acetone) and Witcamine AL 42-12 (58 g in 40 ml acetone) were first prepared. Equal volumes of these solutions were then combined to form the electrode treating solution. The dye electrodes were submerged in this solution for 20 s and dried by evaporation of the solvent.

3. Silanizing Agents

The use of a silane linkage to couple the inner surface of the diphthalocyanine layer to the tin oxide was briefly investigated with Dynastan IMEO and with Dow Z6020. These commercial products were diluted with methanol-water or ethanol-water solvents to make solutions containing 0.8 to 2.4 wt % of the active ingredient. Tin oxide substrates were dipped several seconds in one of the silanizing solutions and air dried prior to vacuum deposition of the dye.

4. AMPS, PolyAMPS, and Poly(ethylene glycols)

The AMPS, polyAMPS, and PEG additives were all water-soluble. A weighed quantity of each was dissolved in water to make a convenient stock solution. The additive was then incorporated by dilution in the 1M KCl electrolyte.

D. EXPERIMENTAL CELLS

The cells were an improved version of those used in a previous Navy project.[4] Photographs of the separate parts and a set of assembled cells are shown in Figures 2 and 3, respectively. The components included a glass housing, which was a purchased Klett colorimeter cell, the working (display) electrode, counter, and reference electrodes. The design features a reusable Teflon lid, which provides better sealing, easy assembly and disassembly, and improved appearance.

The dye electrode was positioned as required for later placement of the cell in the spectrometer. The final assembling and filling of the cells was done in a Vacuum Atmospheres HE-43 Glove Box filled with helium which typically contained about 5 ppm oxygen.

E. INSTRUMENTATION

The electrochemical instrumentation assembly included an EG&G/Princeton Applied Research (PAR) Model 173 Potentiostat/Galvanostat with a PAR Model 179 Coulometer, a PAR Model 175 Universal Programmer, a Houston Instruments Model 2000 X-Y Recorder, and a Tektronix 7623A Oscilloscope with a 7B53A Dual Time Base, 7A22 Differential Amplifier, and other accessories. Two of the programmed potentiometer setups were assigned to long-term cycling of the cells, and a third was available for cyclic voltammetry and other short-term experiments.

The pulse timing system of the PAR instruments provided for cycling the test electrodes between two voltage levels. This capability was extended by the addition of three Hewlett-Packard Model 59308A Timing Generators which had been slightly modified for compatibility with the PAR equipment. It was then possible to select four independent pulse times in a 4-level potentiostatic cycling routine.

Interconnect circuitry was designed and fabricated to cycle, potentiostatically, as many as six electrochromic cells in parallel on a single PAR assembly. Extended leads were also provided for cycling groups of cells housed in the glove box.

Additional equipment included a Beckman UV 5230 Spectrophotometer, on which visible-range absorption spectra of the dye films were recorded, before and during activation, and a Beckman Model Phi 71 precision pH meter. A variable sine-wave

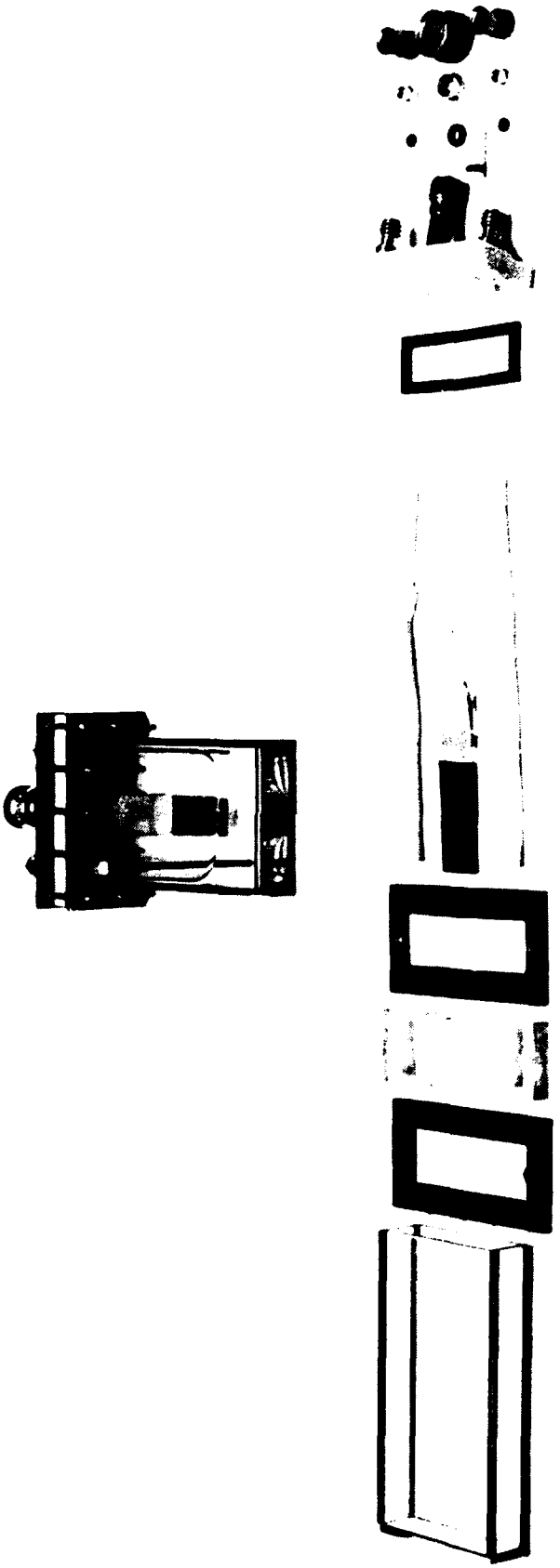


Figure 2. Electrochromic Cell Assembly

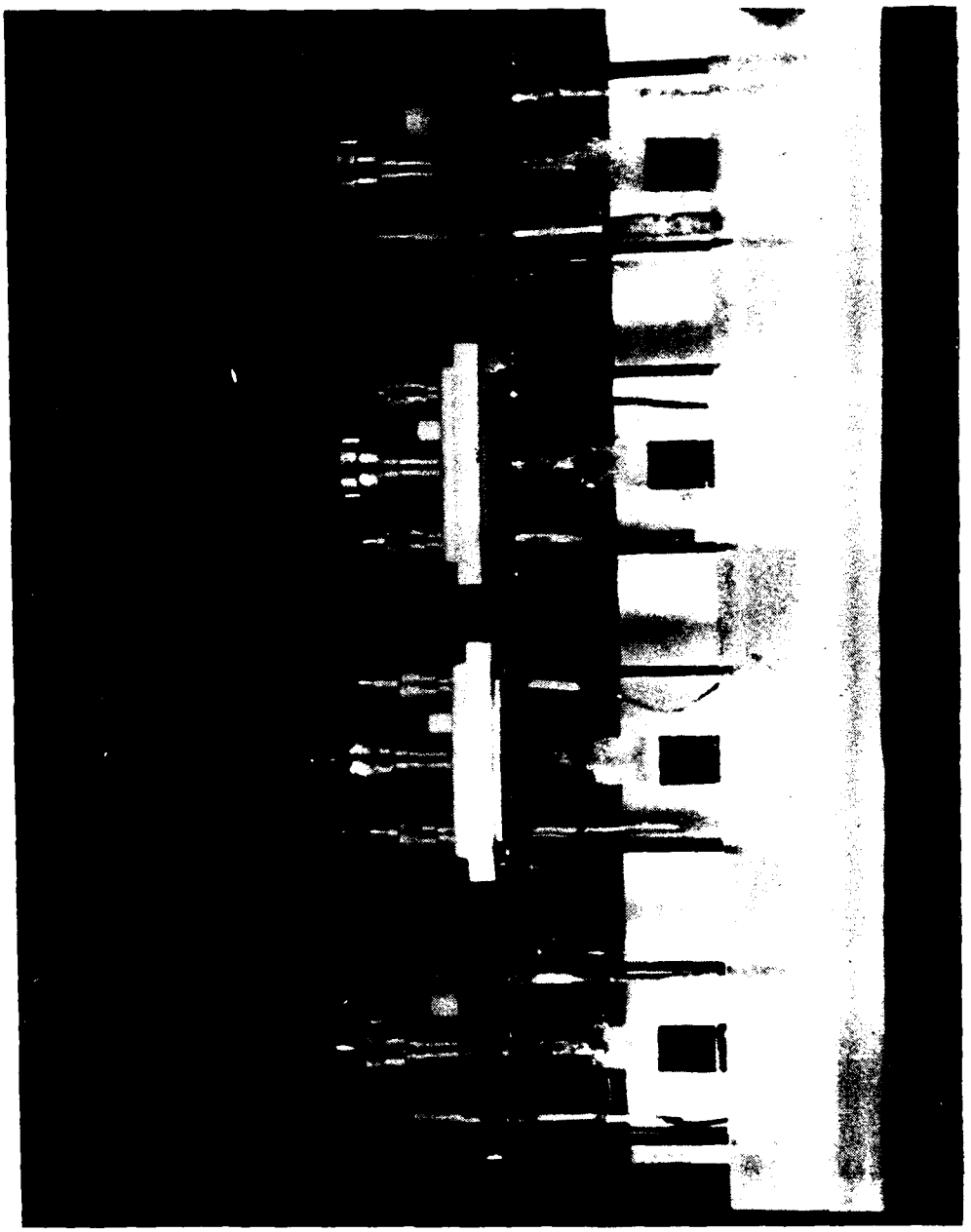


Figure 3. Group of Cells for Cycle-Life Determination

voltage source was employed, with the oscilloscope, for resistance measurements on an insulator-supported dye film.

F. CYCLE-LIFE MEASUREMENTS

1. Display Electrodes

Groups of closely related cells containing dye electrodes were cycled in parallel by application of constant-potential pulses to the display electrodes. Each cell current was also carried by the counter electrode of that cell. All of the display electrodes were on a common connector leading to the working-electrode input of the potentiostat, and all of the counter electrodes were connected in common to the counter-electrode input. If the reference electrodes were connected together, however, the system became unstable because the potentiostat over-reacted to minor differences in control requirements of the various cells. For that reason, one reference electrode in each group of cells was chosen as the control electrode, and only that electrode was connected to the reference position on the potentiostat. The other reference electrodes in the set were left floating during the cycling process but remained available for controlling the input signals to those cells when they were removed from the cycling line for individual evaluation.

The 2-level cycling routine consisted of 1 s at a constant anodic potential and 1s at a constant cathodic potential, or 2 s/cycle. For the orange/green or orange/blue-green transition of lutetium diphthalocyanine, the levels usually were +0.95 V and -0.20 V vs Ag/AgCl. In the neutral electrolytes, the dye is normally green at -0.20 V, with the same oxidation state as the original vacuum deposited film. At pH < 4, however, the stable phase at -0.20 V is the blue-green, or "light blue" form, which is 1-electron reduced with respect to the green.[4] The hue at either steady potential could vary in the course of the cycling experiment if the conversion were incomplete. For orange/blue cycling, the voltage levels were +0.95 V and -0.35 V in acidic electrolytes and +0.95 V and -1.20 V in neutral electrolytes. These cathodic levels caused some of the darker blue products to form, but not enough for complete 2-electron reduction beyond the blue-green (light blue) stage.

A few experiments were done with 4-level cycling so that most of the electrode reaction occurred in the first 0.1 s, anodic or cathodic, and the electrode remained essentially at a null, or zero-current, condition for the remaining 0.9 s.[1] The null potentials were set by trial by observing the current transient on the oscilloscope. A typical sequence was: 0.1 s at +1.30 V, 0.9 s at +0.90 V, 0.1 s at -1.00 V, and 0.9 s at -0.05 V. The "spike" voltages applied for only 0.1 s served to overcome the ohmic drop and accelerate the electrochemical kinetics. As the reaction approached completion, the extra voltage for the resistive components was no longer needed. This routine was less destructive than the 2-level procedure but was somewhat tedious to control in long-term testing under a variety of conditions. Hence it was not used extensively in the present work.

The dye electrodes were characterized initially by their visible absorption spectra in the dry state. During life testing, the cells were removed from the cycling circuit at intervals so that several measurements could be made on the individual display electrodes. These included:

(a) Steady-state absorption spectra at potentials corresponding to the green or blue-green and orange conditions.

(b) Transient charge transferred in and out of the film as a function of time from 0 to 1 s, measured on the Houston Instruments X-Y recorder.

(c) Optical absorption transients from 0 to 1 s, and in some cases to 10 s, observed on the pen recorder of the spectrometer at a full-scale period of 0.5 s.

2. Counter Electrodes

Experiments designed for direct testing of counter electrodes were done on cells with the same types of glass housings and feed-through hardware. These cells contained no dye electrodes but were equipped, instead, with a test (working) electrode, an auxiliary current-carrying electrode, and a reference electrode, all three having the same chemical composition--either Ag/AgCl or Pb/PbF_2. For convenience in setting the

instruments, the test electrodes were much smaller (0.1 to 0.2 cm^2) than the counter electrodes described in Part B-2 of this section.

The current transient experienced by a counter electrode during its use in a display cell resembles that of a capacitor being charged through a resistance; the usual form consists of a sharp rise followed by an exponential decay. To simulate such operation, the cells in the counter-electrode cycling tests were subjected to controlled-current pulses, 0.1 s anodic and 0.1 s cathodic. Two pulse routines were used. The first was a square-wave signal which provided current densities in the range of 2 to 10 mA/cm^2 on the test electrodes. The second was a saw-tooth, which applied peak current densities up to 13 mA/cm^2 for Ag/AgCl and 21 mA/cm^2 for Pb/PbF_2. For efficient collection of data, groups of similar experimental cells were cycled in series at the same total current.

The counter-electrode performances were characterized individually during cycling by measuring the voltage transients between the test and reference electrodes on the oscilloscope, using a differential-input amplifier. The cycling was begun in each case with the test electrodes at 50 % state-of-charge.

G. SUPPLEMENTAL TECHNIQUES

1. Dye-Film Resistance Measurements

To investigate the effect of propylene glycol (PG) as a possible plasticizer for the dye film, the resistance of a lutetium diphthalocyanine film was examined on a nonconductive sapphire substrate. The vacuum deposited film was contacted by two gold-strip electrodes ~ 1.3 cm long and 0.3 cm apart. The resistance parallel to the surfaces of the film was measured by an ac current method in which the sample was connected in series with a variable sine-wave voltage source and the 1 megohm input resistance of the oscilloscope. The total resistance of the sample plus 1 megohm was found from the ratio of the peak-to-peak voltage output of the source to the peak-to-peak current measured on the oscilloscope.

The film resistance at room temperature was determined in the green and orange states under dry nitrogen and under nitrogen saturated with PG vapor. The

oxidized (orange) state was produced for this experiment by exposing the green form briefly to gaseous chlorine.

2. Cyclic Voltammetry

Cyclic voltammetry with linear variation of the applied potential was employed primarily as a screening method to distinguish promising dye/electrolyte combinations from those that switched with greater difficulty. With this method, a ramp voltage was applied to the display cell, first in one direction and then in reverse, returning to the starting point, while current-voltage curves were recorded. The scanning rate usually was varied from 10 to 100 mV/s. Cyclic voltammetry was applied to lutetium diphthalocyanine electrodes in several aqueous media containing AMPS or related materials and in a KCl-propylene glycol electrolyte. It was also used to examine the neodymium diphthalocyanine electrode and correlate its color responses with the driving voltage.

3. Analytical Methods

Supporting analytical methods used to characterize the dye films and other solid materials included Auger spectroscopy, infrared spectroscopy, and x-ray powder crystallography.

III. RESULTS AND DISCUSSION

Part A of this section presents the results of cycle-life studies and related experiments on lutetium diphthalocyanine display electrodes in the orange/green, orange/blue-green, and orange/blue switching modes. Improvement of the red color by the use of neodymium diphthalocyanine is also documented. The investigation of silver/silver chloride and lead/lead fluoride counter electrodes is reported in Part B, and conclusions from the experimental investigation are summarized in Part C.

A. DISPLAY ELECTRODES

1. Cycle-Life Determination

The experimental conditions and results for life testing of individual cells, identified by display electrode numbers, are recorded in Tables 1-6. The cycle life is reported on the basis of switching charge q for all of the measurements. For the orange/green or orange/blue-green series, the tables also give the apparent life based on absorbance at 665 nm, measured at the potential of -0.10 V, which corresponded to the green or blue-green state, depending on pH. For brevity, the symbol A_G is used in the tables and figures to represent the absorbance in either the green or the blue-green state.

The symbol A_{Dry} represents the absorbance at the 665-nm peak for the original green film. This absorbance provides an approximate measure of the dye-film thickness, or weight per unit area W, through the relationship[1]

$$W = 14.5\ A_{Dry} \tag{1}$$

where W is in $\mu g/cm^2$. If the film were nonporous and had a density* of 1.55 g/cm^3, the thickness d in μm would then be given by

$$d = 0.0935\ A_{Dry} \tag{2}$$

*Estimated as the crystal density of neodymium diphthalocyanine.[9]

TABLE 1

LIFE DATA FOR $LuPc_2$ FILMS ON DIFFERENT SUBSTRATES WITH ORANGE/GREEN CYCLING IN KCl AND KCl-HCl ELECTROLYTES

	Electrolyte			Electrode		Cycle Life[a,b]	
Substrate	Primary	Additive	pH	No.	A_{Dry}	Based on q	Based on A_G
SnO_2/Glass	1M KCl	--	~ 7	1	1.13	4.7×10^4	2.8×10^4
				2	1.10	2.1×10^4	1.9×10^4
				3	1.09	4.1×10^3	3.7×10^4
				4	1.78	$\sim 1 \times 10^4$	2.8×10^4
SnO_2/Glass	1M KCl	0.033M HCl[c]	1.8[c]	5	1.52	2.5×10^5	$>4 \times 10^6$
ITO/Glass	1M KCl	--	~ 7	6	2.11	2.0×10^4	2.9×10^4
				7	1.52	7.9×10^3	2.2×10^4
				8	1.61	5.9×10^3	2.4×10^4
ITO/Polyester	1M KCl	--	~ 7	9	2.06	1.7×10^5	1.5×10^5
				10	2.00	3.2×10^4	1.0×10^5
				11	1.52	1.7×10^4	2.8×10^4

[a]Measurement Conditions: Cycle 1 s at 0.95 V and 1 s at -0.20 V vs Ag/AgCl
Spectra at 0.70 V and -0.10 V
A_{Dry} and A_G: A_{665} -A_{800}

[b]Life Evaluation: 50 % decrease in q at 1 s or A_G

[c]Orange/Blue-Green

TABLE 2

LIFE DATA FOR $LuPc_2$ FILMS WITH 4-LEVEL ORANGE/GREEN CYCLING IN KCl ELECTROLYTE

	Electrolyte			Electrode		Cycle Life[a,b]	
Substrate	Primary	Additive	pH	No.	A_{Dry}	Based on q	Based on A_G
SnO_2/Glass	1M KCl	--	~ 7	12	0.821	4.6×10^3	$>10^6$
				13	1.14	$\sim 1 \times 10^5$	$\sim 2 \times 10^6$
				14	1.18	1.8×10^4	$\sim 1 \times 10^6$

[a]Measurement Conditions:

Electrode 12: Cycle 0.1 s at 1.00 V, 1 s at 0.70 V, 0.1 s at -1.00 V, 1 s at 0.10 V vs Ag/AgCl
Electrodes 13 and 14: Cycle 0.1 s at 1.30 V, 0.9 s at 0.90 V, 0.1 s at -1.00 V, 0.9 s at -0.05 V
A_{Dry}: $A_{665} - A_{800}$

[b]Life Evaluation: 50 % decrease in q at 1 s or in A_G

TABLE 3

LIFE DATA FOR $LuPc_2$ FILMS WITH NAFION BINDER AND ORANGE/GREEN CYCLING IN KCl ELECTROLYTE

Substrate	Film Additive	Electrolyte			Electrode		Cycle Life[a,b]	
		Primary	Additive	pH	No.	A_{Dry}	Based on q	Based on A_G
SnO_2/Glass	Nafion	1M KCl	--	~ 7	15	1.10	1.5×10^5	4.6×10^5
					16	0.837	1.9×10^5	3.6×10^5
					17	0.882	6.9×10^4	4.3×10^5
ITO/Glass	Nafion	1M KCl	--	~ 7	18	1.02	1.8×10^5	2.8×10^5
					19	1.19	2.3×10^5	$> 10^6$
					20	1.70	1.6×10^5	9.3×10^4
ITO/Polyester	Nafion	1M KCl	--	~ 7	21	2.01	$> 10^5$	$> 10^5$
					22	2.09	$> 10^5$	$> 10^5$
					23	1.53	5.0×10^5	1.2×10^6

[a]Measurement Conditions: Cycle 1 s at 0.95 V and 1 s at -0.20 V vs Ag/AgCl
Spectra at 0.70 V and -0.10 V
A_{Dry} and A_G: $A_{665} - A_{800}$

[b]Life Evaluation: 50 % decrease in q at 1 s or in A_G

TABLE 4

LIFE DATA FOR $LuPc_2$ FILMS WITH ORANGE/GREEN CYCLING IN KCl WITH POLY(ETHYLENE GLYCOL) ADDITIVES

	Electrolyte			Electrode		Cycle Life[a,b]	
Substrate	Primary	Additive	pH	No.	A_{Dry}	Based on q	Based on A_G
SnO_2/Glass	1M KCl	0.001 % PEG (300)[c]	~ 7	24	0.815	2.9×10^3	2.1×10^3
		0.01 %		25	0.778	3.8×10^3	2.7×10^4
		0.01 %		26	1.86	2.0×10^3	5.5×10^4
		0.1 %		27	0.926	4.1×10^4	4.2×10^5
	1M KCl	0.12 % PEG (3350)[c]	~ 7	28	1.84	9.8×10^2	1.1×10^4
		0.99 %		29	1.80	9.1×10^2	2.8×10^4

[a]Measurement Conditions: Cycle 1 s at 0.95 V and 1 s at -0.20 V vs Ag/AgCl
Spectra at 0.70 V and -0.10 V
A_{Dry} and A_G: $A_{665} - A_{800}$

[b]Life Evaluation: 50 % decrease in q at 1 s or in A_G

[c]Molecular weights of PEG in parentheses

TABLE 5

LIFE DATA FOR $LuPc_2$ FILMS WITH ORANGE/BLUE-GREEN CYCLING IN KCl WITH AMPS ADDITIVES

	Electrolyte			Electrode		Cycle Life[a,b]	
Substrate	Primary	Additive	pH	No.	A_{Dry}	Based on q	Based on A_G
SnO_2/Glass	1M KCl	0.005M AMPS	2.5	30	1.11	5.0×10^5	$>10^6$
	1M KCl	0.05M AMPS	1.5	31	1.11	2.0×10^6	$>2.5 \times 10^6$
				32	1.71	2.5×10^6	6.6×10^6
	1M KCl	0.24M AMPS	0.59	33	1.50	3.2×10^6	4.6×10^6
				34	1.58	1.3×10^6	1.7×10^6
				35	1.73	1.4×10^6	3.0×10^6
				36	1.40	1.4×10^6	1.7×10^6
SnO_2/Glass	1M KCl	0.05M poly-AMPS[c]	1.5	37	1.61	3.6×10^6	5.2×10^6
	1M KCl	0.25M poly-AMPS[c,d]	0.59	38	1.33	1.2×10^6 [d]	$> 10^6$ [d]
SnO_2/Glass	1M KCl	0.2M NaAMPS[e]	~ 7[e]	39	0.643	8.3×10^4	4.0×10^5

[a]Measurement Conditions: Cycle 1 s at 0.95 V and 1 s at -0.20 V vs Ag/AgCl
Spectra at 0.70 V and -0.10 V
A_{Dry} and A_G: $A_{665} - A_{800}$

[b]Life Evaluation: 50 % decrease in q at 1 s or A_G

[c]Molarity based on monomer

[d]Gold contact to tin oxide

[e]Orange/Green

TABLE 6

LIFE DATA FOR $LuPc_2$ FILMS WITH ORANGE/BLUE CYCLING IN SEVERAL ELECTROLYTES

	Electrolyte			Electrode		Cycle Life[a,b]
Substrate	Primary	Additive	pH	No.	A_{Dry}	Based on q
SnO_2/Glass	1M KCl	--	~ 7	40	1.51	3.2×10^4
	1M KCl	--	~ 7	41	1.86	5.6×10^4
	1M KCl	0.005M NaAMPS	6.7	42	1.45	3.6×10^4
SnO_2/Glass	1M KCl	0.25M AMPS	0.59	43	1.68	3.5×10^3
	1M KCl	0.25M AMPS	0.59	44	1.56	6.0×10^3
	0.2M HCl	--	0.73	45	1.57	3.0×10^4
	0.2M HCl	--	0.73	46	1.63	7.8×10^3

[a]Measurement Conditions:

Electrodes 40 through 42: Cycle 1 s at 0.95 V and 1 s at -1.20 V vs Ag/AgCl
Electrodes 43 through 46: Cycle 1 s at 0.95 V and 1 s at -0.35 V
A_{Dry}: $A_{665} - A_{800}$

[b]Life Evaluation: 50 % decrease in q at 1 s.

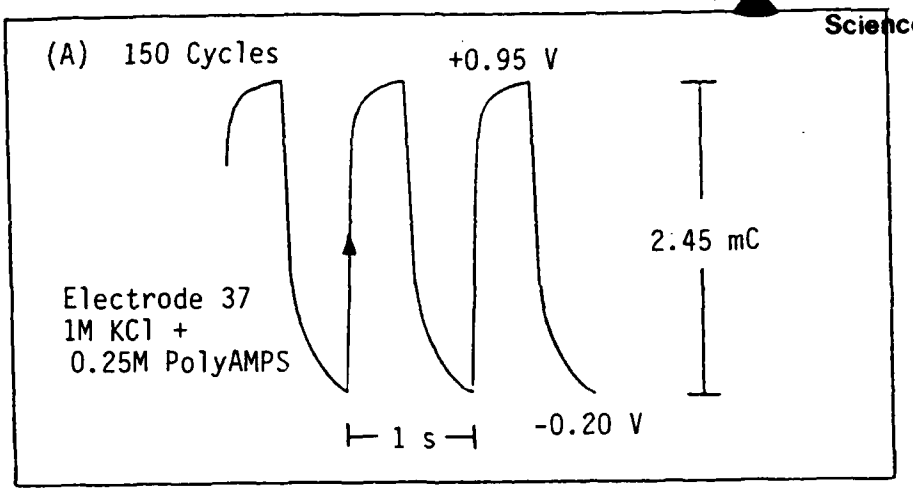
Equation 1 is not exact in the present work because heating of the substrate during the dye deposition was not precisely controlled. It is known from another Rockwell study that variable heating and subsequent exposure to air can affect the absorption peak height in the uncycled green state.[10] Substrate heating is generally beneficial, however, in extending the cycle life of the dye film.

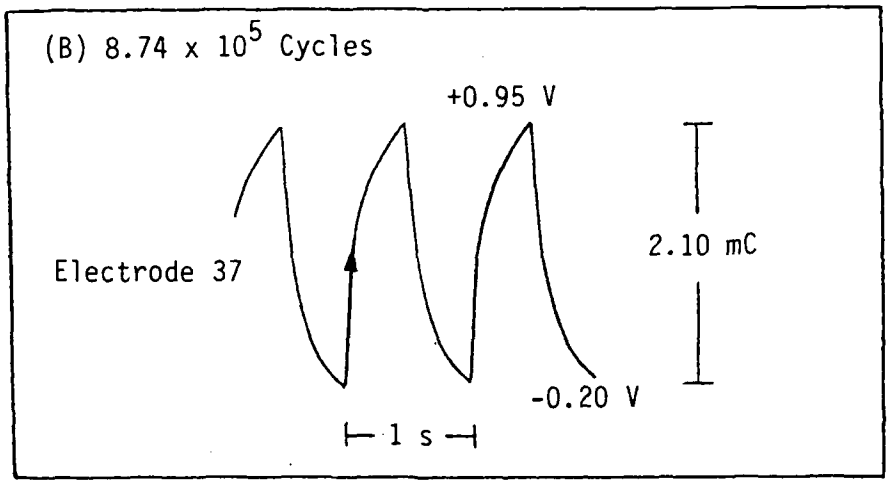
The pH values for the acidic electrolytes were measured directly. For the "neutral" solutions, the pH measured in air was typically about 6 due to the presence of carbon dioxide; this is a normal situation. On the removal of air for life testing, the pH in those electrolytes was near 7.

Before the results are discussed in detail, several features of the measurements will be recalled. The switching charge q is a dynamic quantity, read at a time of 1 s on a pen-recorded charge transient of the type shown in Figure 4. Although most of the switching, or charge-transfer, reaction is normally completed in less than 50 ms with a fresh film,[3] the process tended to become slower on prolonged cycling. Eventually, the lower speed was reflected in a smaller charge measured at 1 s.

The absorbances A_G and A_R are steady-state quantities taken from complete visible spectra for the green (or blue-green) and the orange states, respectively. These were recorded after the electrode stood several minutes at constant potential and the current had reached essentially zero. The stationary potentials (0.70 V for orange and -0.10 V for green or blue-green) were set at lower magnitudes than the driving pulses (0.95 and -0.20 V) because the latter included resistive voltage drops present only under current flow. Examples of spectra in green, blue-green, and orange conditions are shown in Figure 5. The tabulated A_G and A_R are net values at 665 nm, obtained by subtracting the low absorbances at 800 nm from the total values; this was done to circumvent the effects of occasional baseline shifts due to light scattering or other factors.

While the charge q represents the amount of dye actually switching within 1 s after a potential pulse was applied (plus any background charge), the absorbance difference $A_G - A_R$ is a measure of the amount of dye that was still switchable on long standing. Where this difference fell below its initial value, some of the dye had been lost, mechanically or chemically, or had become isolated from the electrode circuit so that it no longer could be switched.





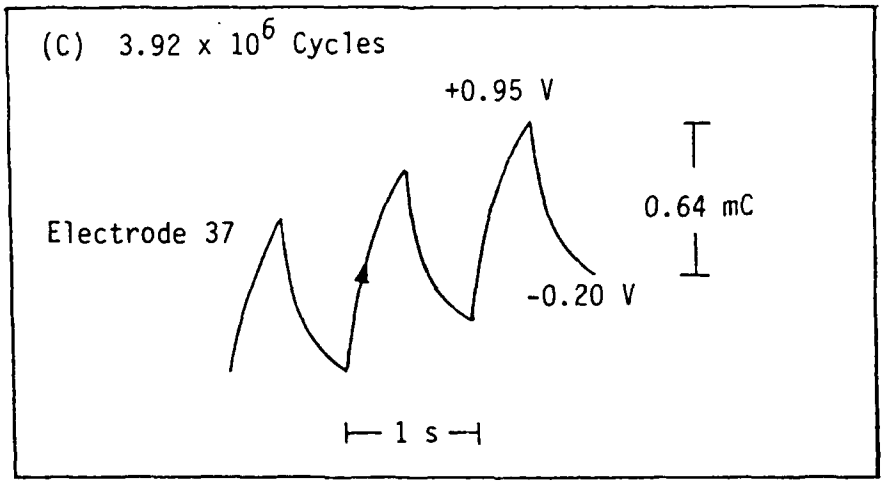


Figure 4. Switching Charge Transients in Early and Later Cycling Stages

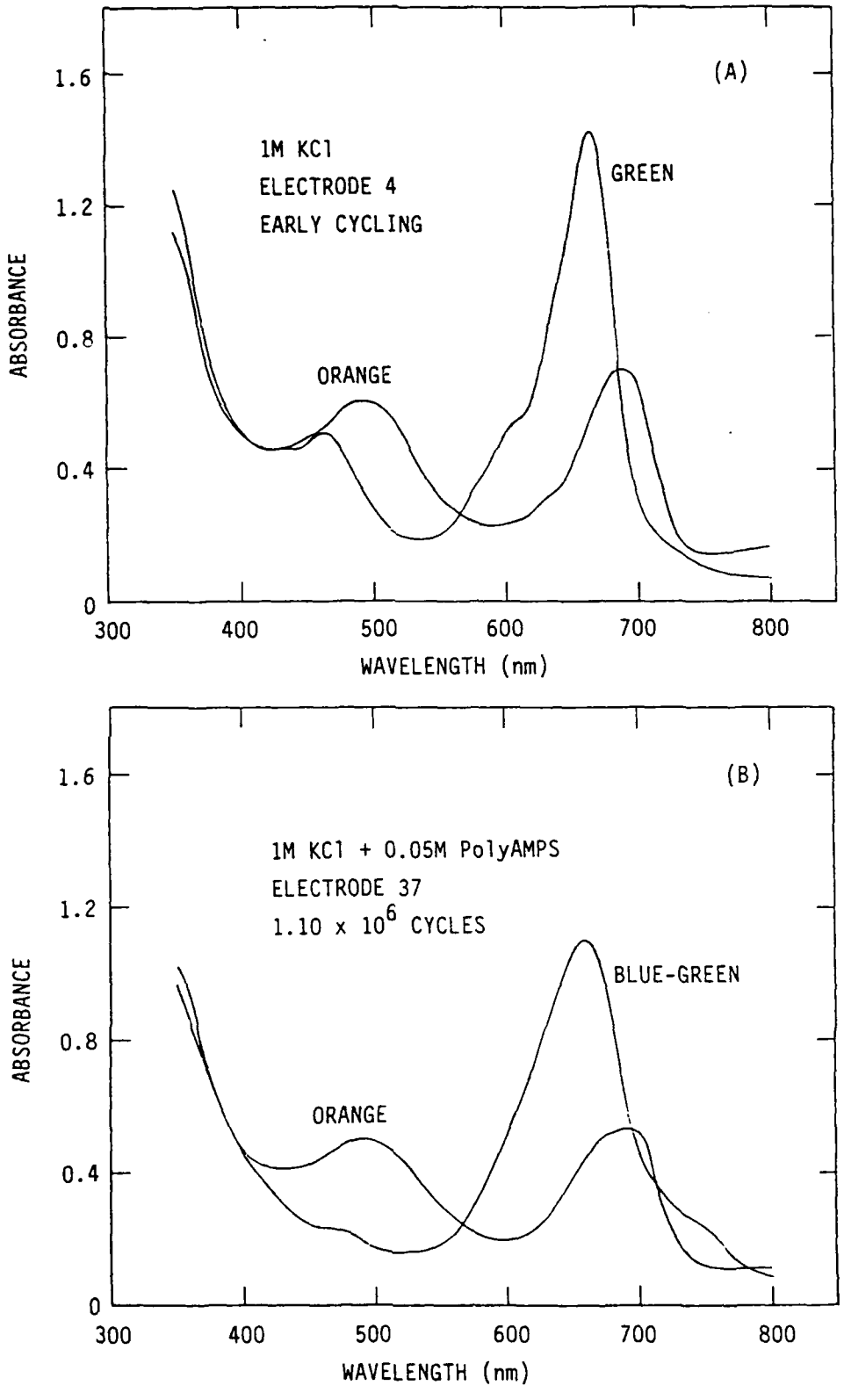


Figure 5. Absorption Spectra at Constant Potentials

Optical transients, illustrated by Figure 6, were also recorded on the Beckman spectrometer at 665 nm in many cases. These curves were independent of background current or charge. Figure 6 confirms the slowing of the orange/blue-green electrochromic process with cycling. It should be noted, however, that the optical transients measurements were limited by the response time of the pen-recording instrument, which was about 500 ms full-scale. For that reason, they were not relied upon as a primary characterization of electrode behavior. Transient measurements on lutetium diphthalocyanine electrodes in the millisecond range, made with different instrumentation, were reported in two previous Rockwell investigations, where time constants for the orange/green process in KCl at an early stage of cycling were found to be on the order of 10 to 25 ms.[3,12]

Representative plots of the orange/green or orange/blue-green switching charge and the corresponding absorbances as functions of total cycles are shown for various experimental conditions in Figures 7-15. Switching-charge plots for the less extensive orange/blue cycling experiments are given in Figure 16.

The plotted quantity q/q_{init} is the ratio of the charge q determined after a given number of cycles to the charge q_{init} found at an early stage--usually 150 cycles. Typically, q_{init} was in the range of 1 to 3 mC. The cycle life based on q was taken at the time when $q/q_{init} = 0.5$, and the life based on absorbance (Tables 1-6) was taken where $A_G = 0.5$. The two evaluation methods gave consistent results in many instances. It is obvious, however, that an electrode failing to switch could give an erroneous long-life reading based on A_G alone. Both the charge and absorbance plots are useful to identify the failure mechanism, but the life evaluation based on charge is considered more significant.

2. Failure Modes in Orange/Green Cycling

Table 7 summarizes the life data and probable failure mechanisms in orange/green cycling. It was found that the dye-electrode behavior could be classified according to three predominant failure mechanisms, which correlated with pH and the types of additives present. These were (a) bleaching, probably chemical in nature, (b) gradual loss of adhesion between the dye film and the electrode or between regions within the dye film, and (c) corrosion of the electronic contact between the transparent

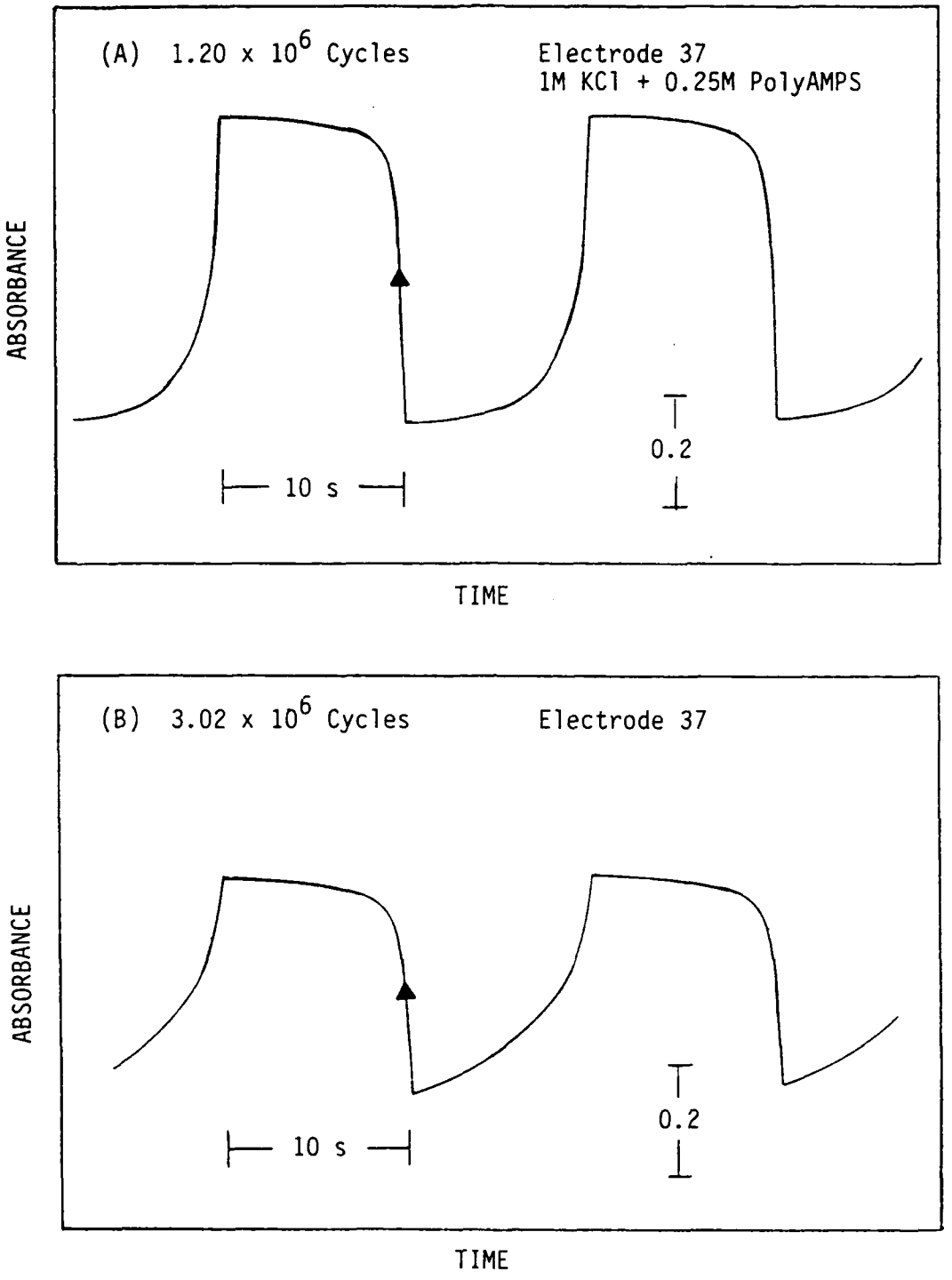


Figure 6. Optical Transients at Different Cycling Stages

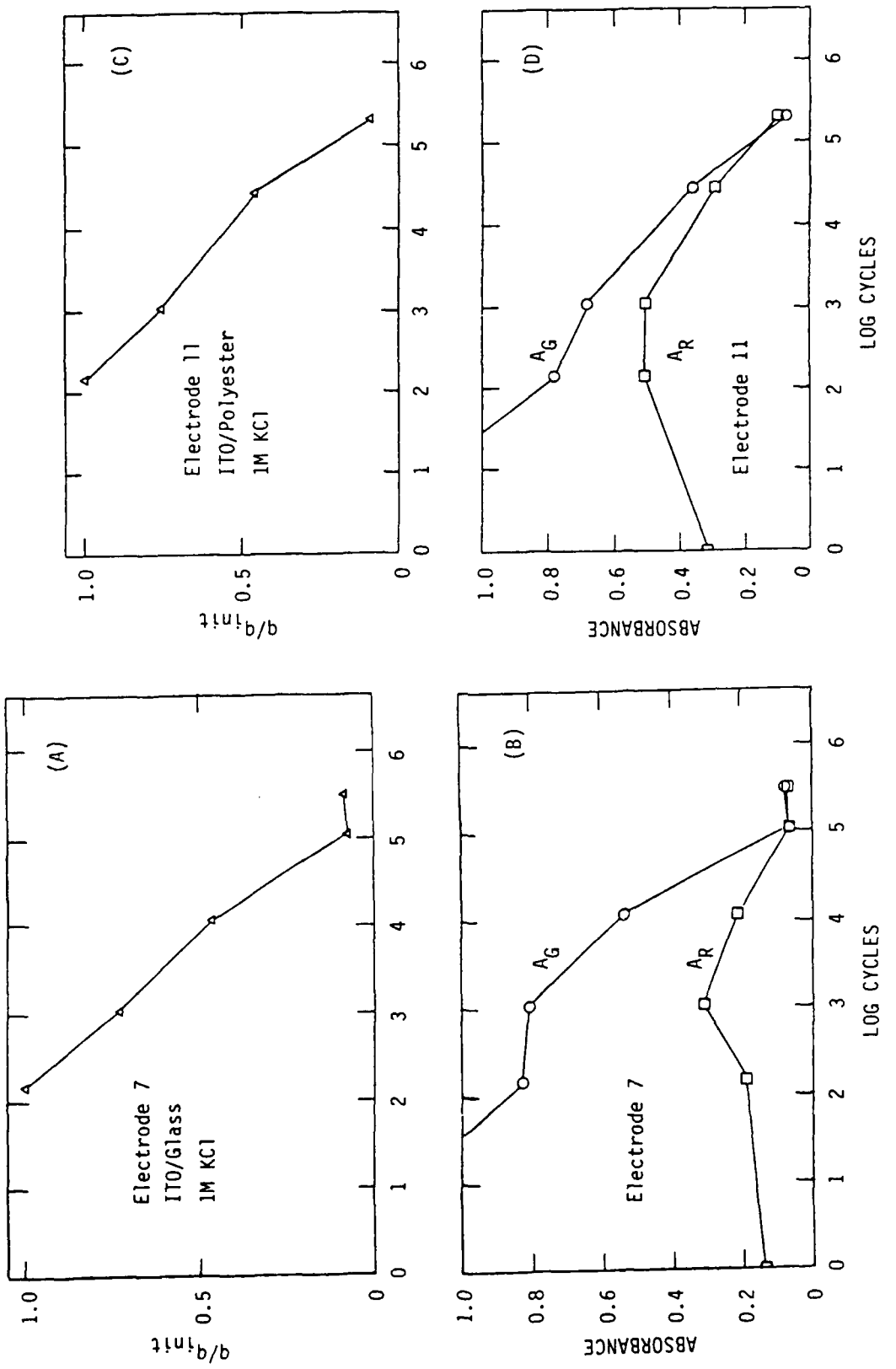


Figure 7. Charge and Absorbance Variations During Orange/Green Cycling with Different Substrates in KCl

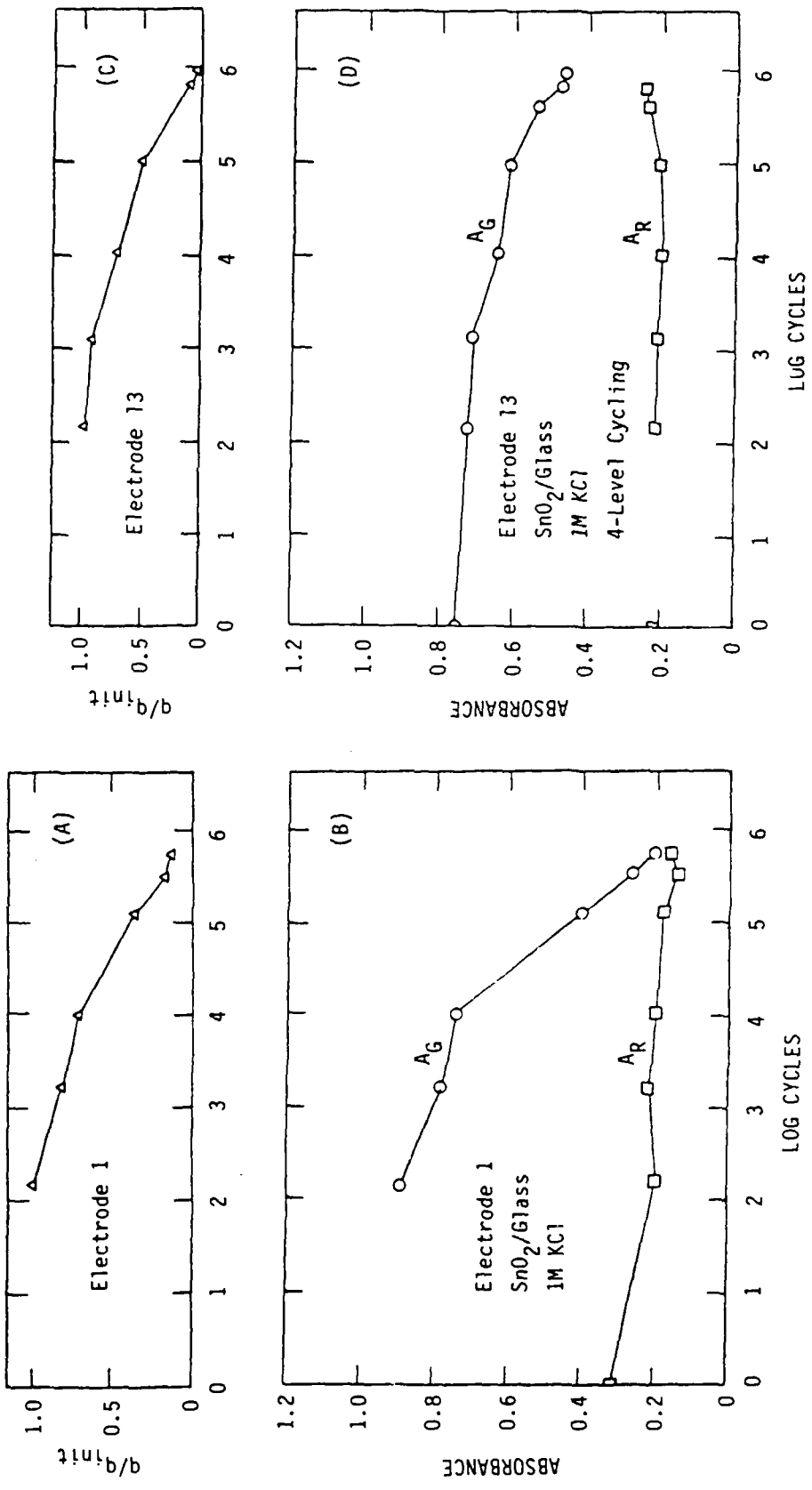


Figure 8. Charge and Absorbance Variations During Orange/Green Cycling with 4-Level Voltage-Pulse Routine

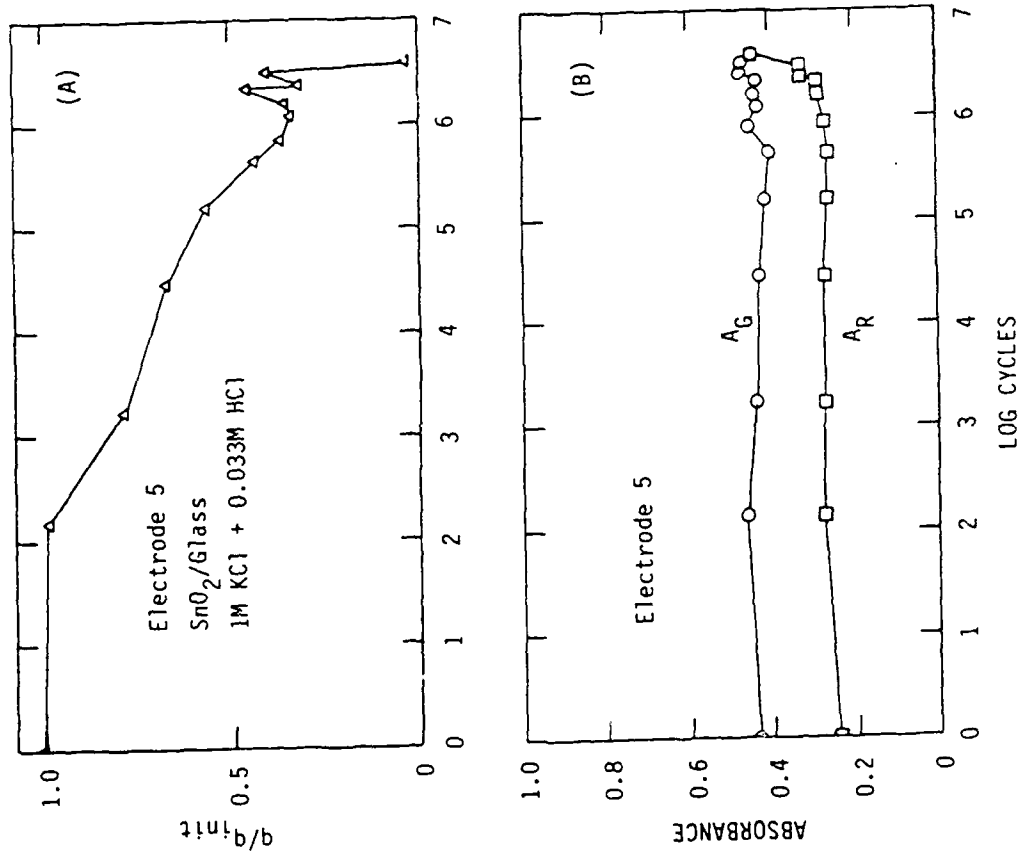


Figure 9. Charge and Absorbance Variations During Orange/Blue-Green Cycling in KCl-HCl Electrolyte

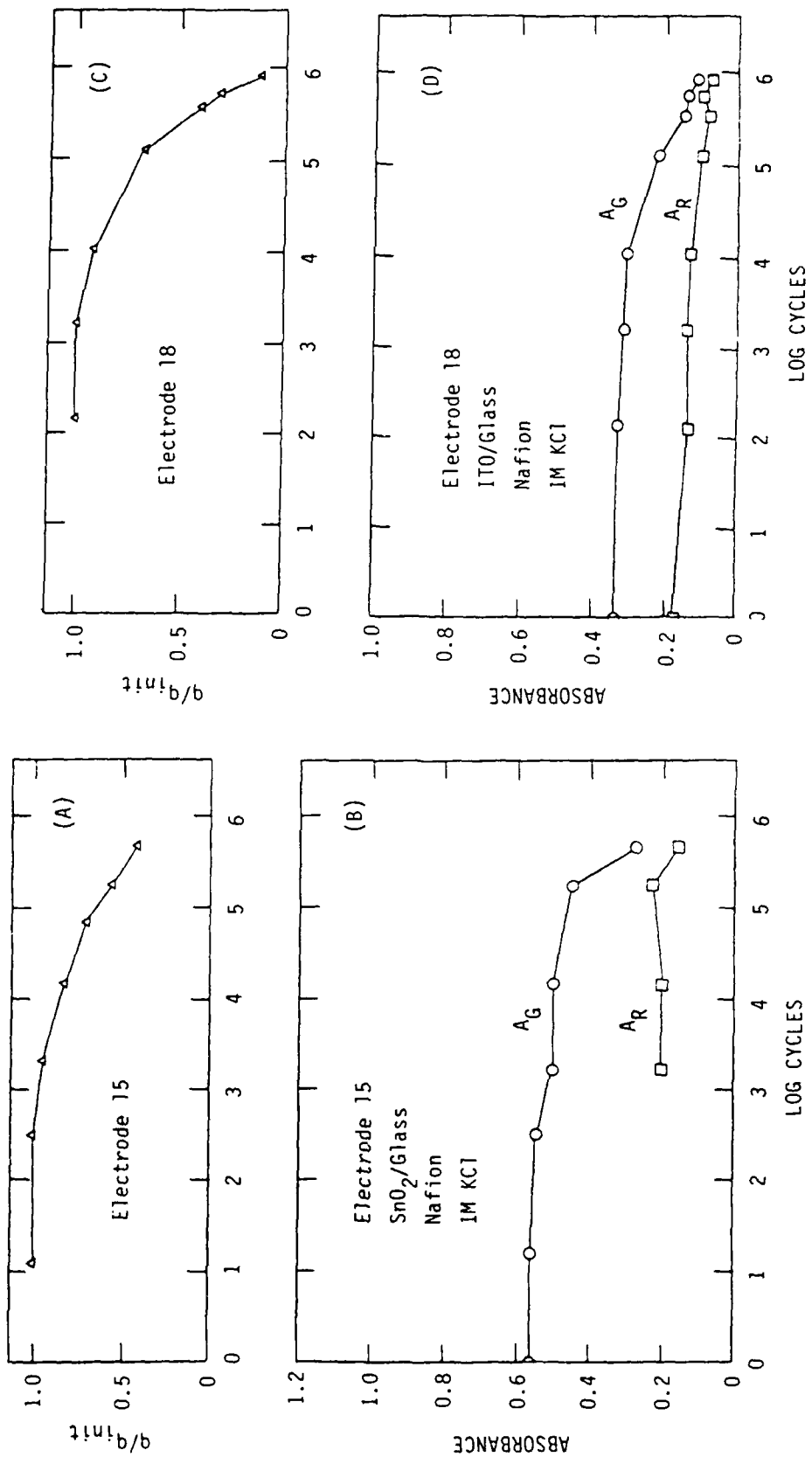


Figure 10. Charge and Absorbance Variations During Orange/Green Cycling of Electrodes with Nafion Binder on SnO_2/Glass and ITO/Glass

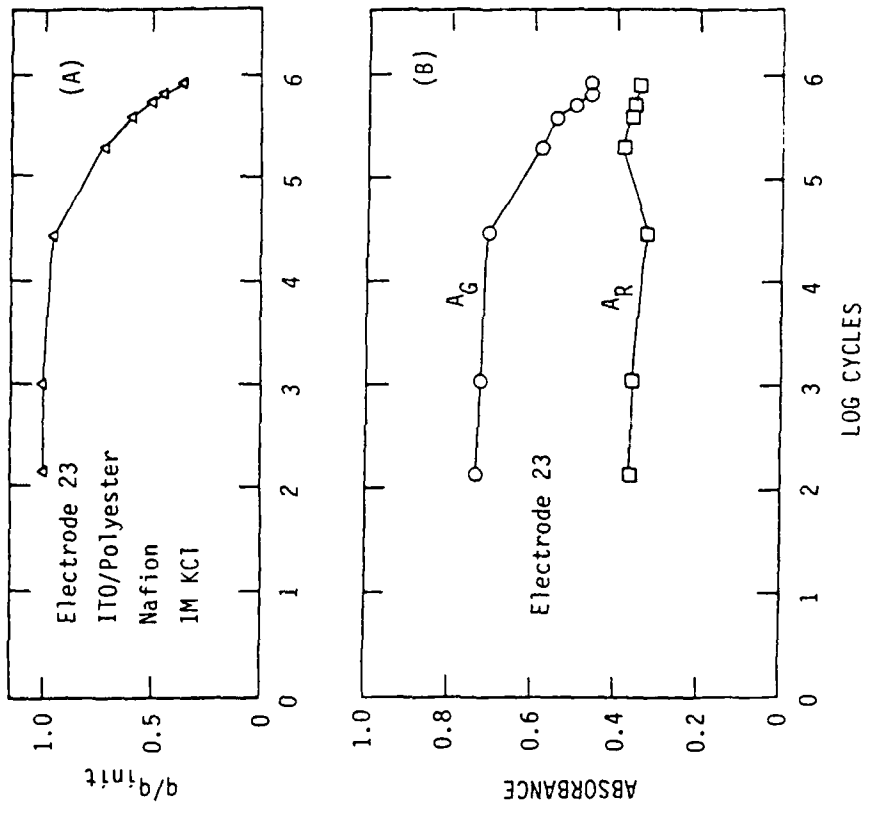


Figure 11. Charge and Absorbance Variations During Orange/Green Cycling of Electrodes with Nafion Binder on ITO/Polyester

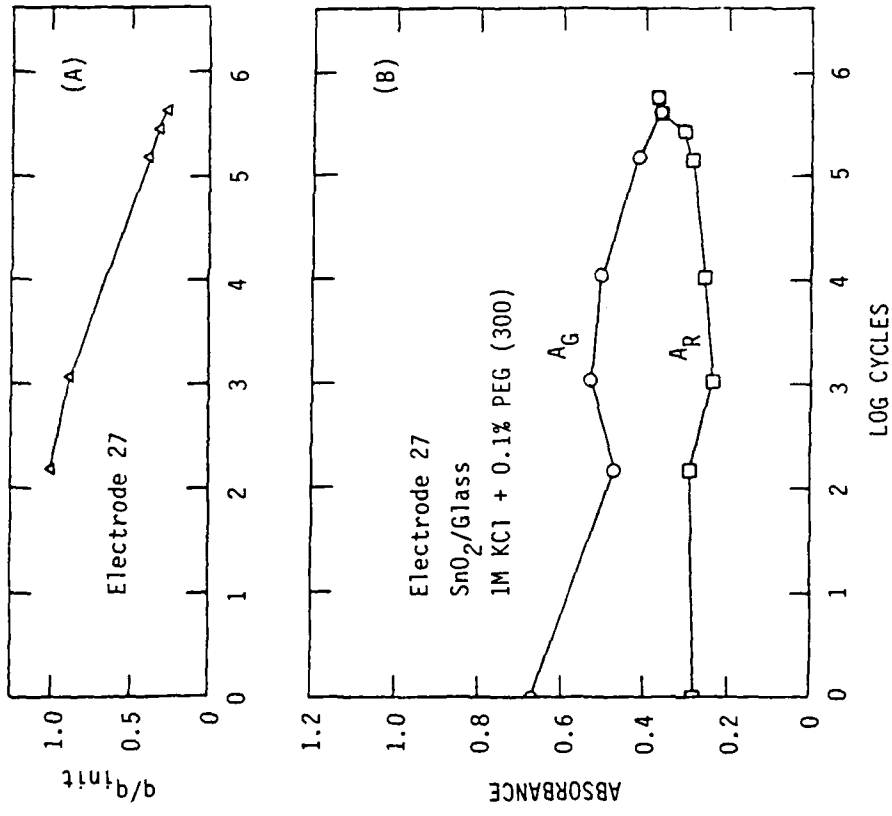


Figure 12. Charge and Absorbance Variations During Orange/Green Cycling with PEG (300) in KCl

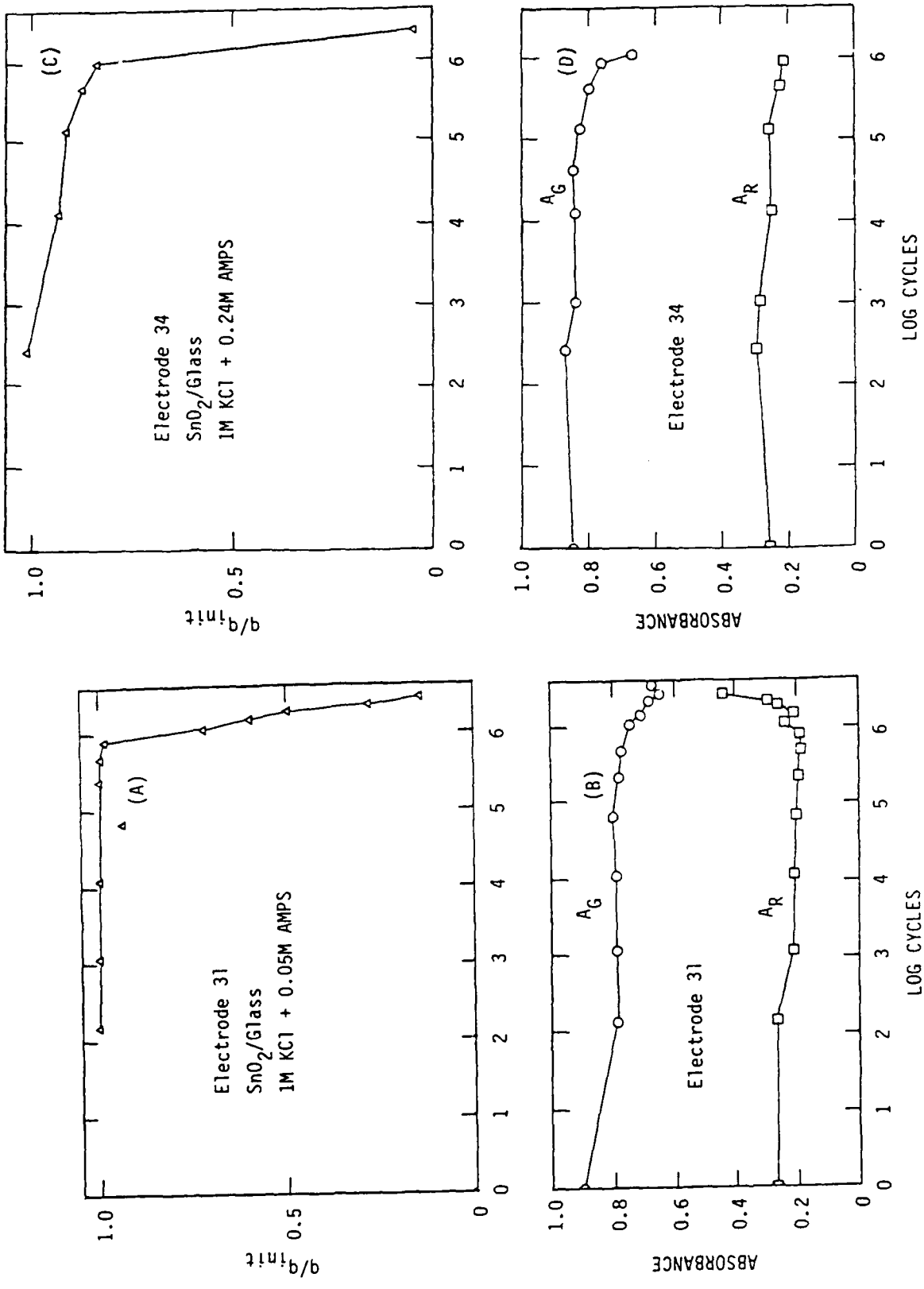


Figure 13. Charge and Absorbance Variations During Orange/Blue-Green Cycling in AMPS-KCl Electrolytes

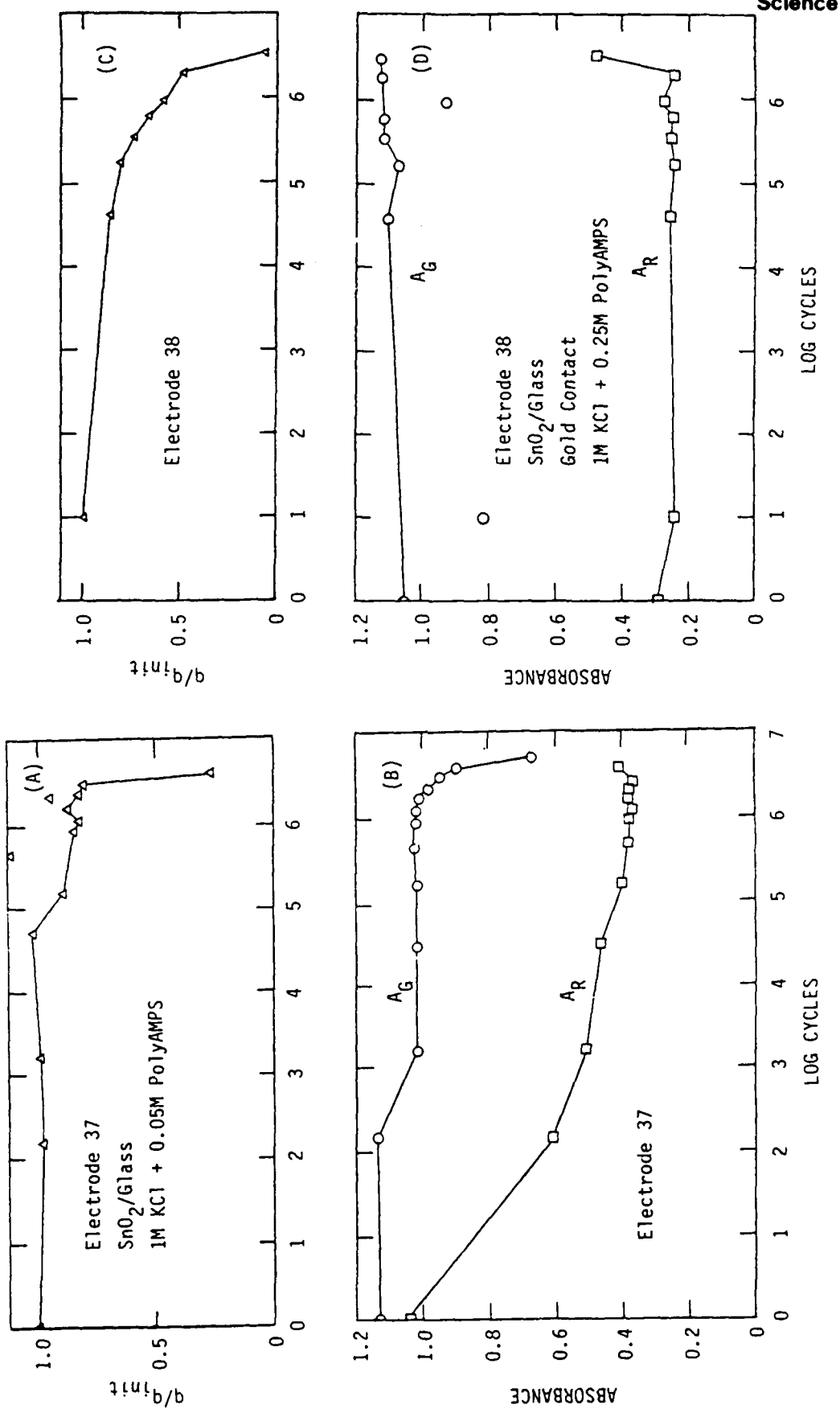


Figure 14. Charge and Absorbance Variations During Orange/Blue-Green Cycling in PolyAMPS-KCl Electrolytes

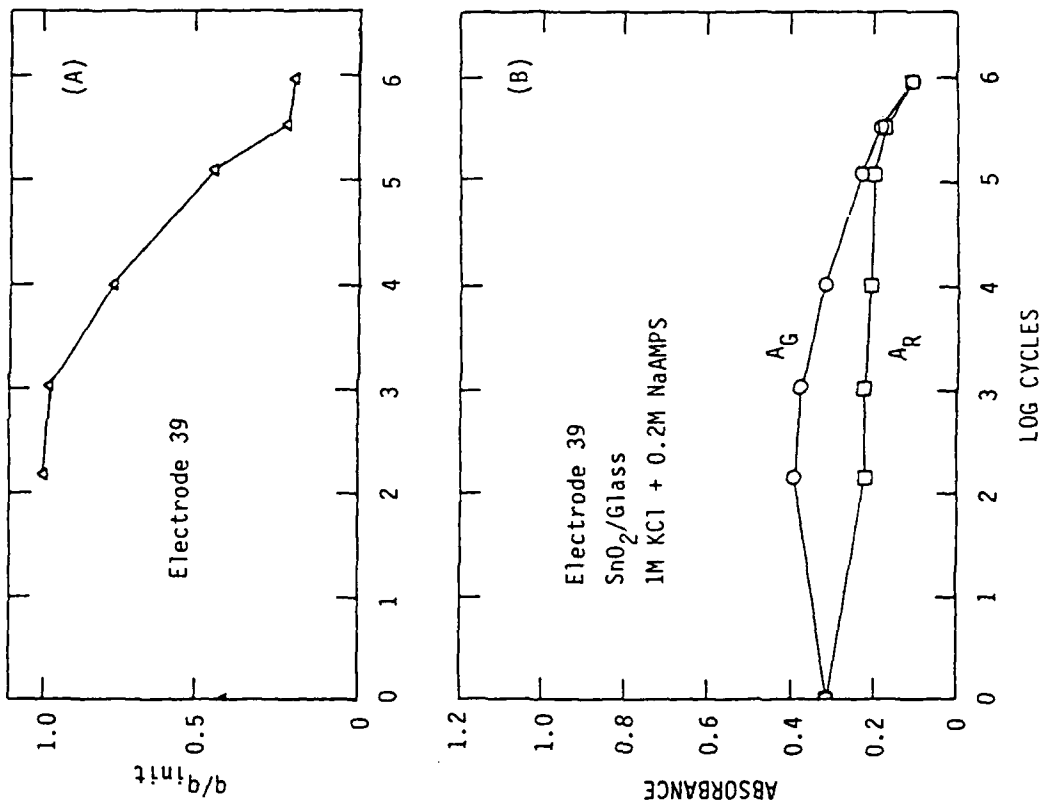


Figure 15. Charge and Absorbance Variations During Orange/Green Cycling in NaAMPS-KCl Electrolyte

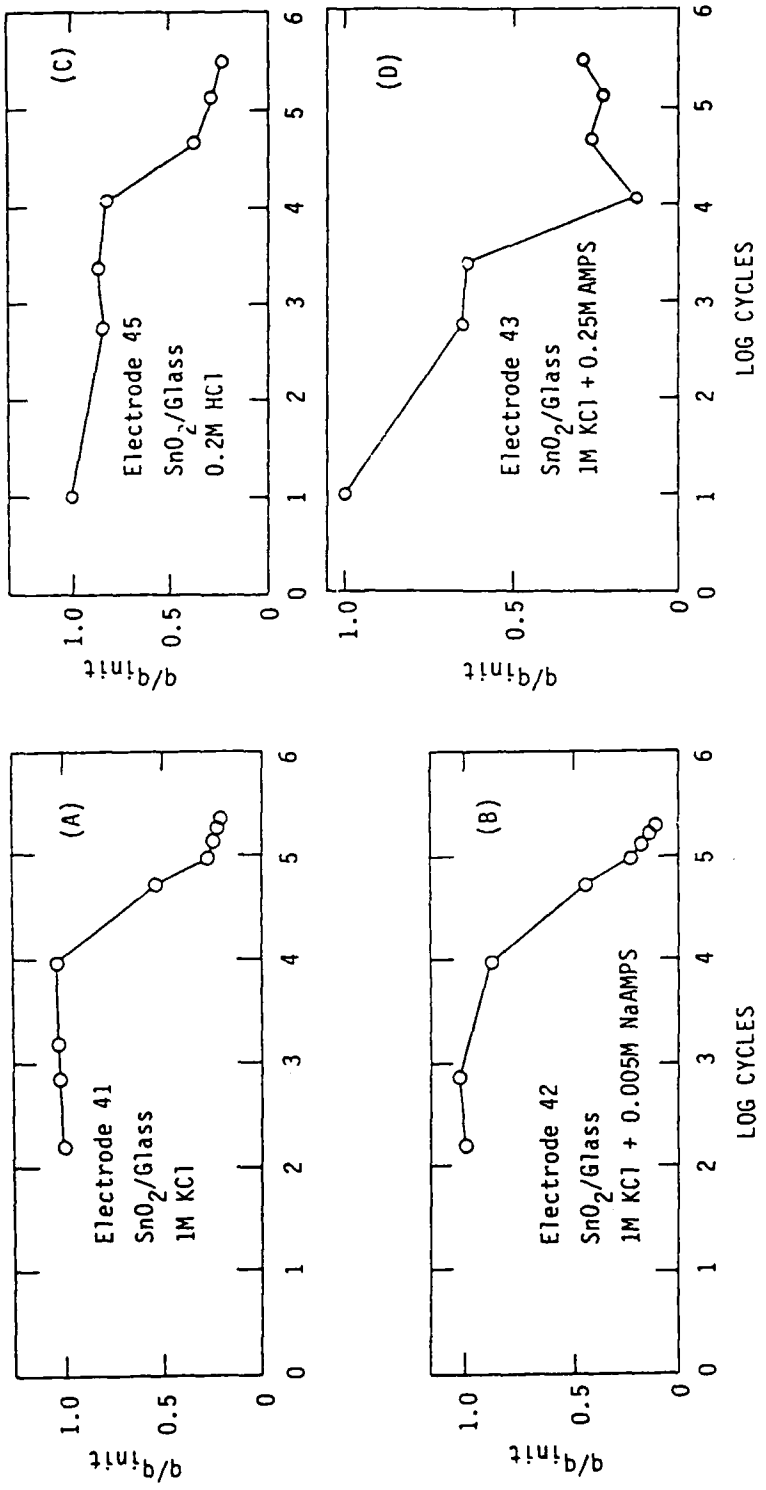


Figure 16. Charge Variations During Orange/Blue Cycling in Several Electrolytes

TABLE 7
SUMMARY OF LIFE DATA FOR $LuPc_2$ FILMS WITH ORANGE/GREEN OR ORANGE/BLUE-GREEN CYCLING[a]

Substrate	Additives		pH	Electrode	Cycle Life Based on q	Probable Failure Mechanism
	Film	1M KCl Soln				
SnO_2/Glass	--	--	~ 7	1	4.7×10^4	Bleaching
ITO/Glass	--	--	~ 7	7	7.9×10^3	Bleaching
ITO/Polyester	--	--	~ 7	11	1.7×10^4	Bleaching
SnO_2/Glass	Nafion	--	~ 7	15	1.5×10^5	Bleaching; loss of adhesion
ITO/Glass	Nafion	--	~ 7	18	1.8×10^5	Bleaching; loss of adhesion
SnO_2/Glass	--	0.12% PEG(3500)	~ 7	28	9.8×10^2	Film or interfacial resistance[b]
SnO_2/Glass	--	0.2M NaAMPS	~ 7	39	8.3×10^4	Bleaching
SnO_2/Glass	--	0.24M AMPS	0.59	33	3.2×10^6	Contact corrosion
SnO_2/Glass	--	0.05M PolyAMPS	1.5	37	3.6×10^6	Contact corrosion
SnO_2/Glass	--	0.033M HCl	1.8	5	2.5×10^5	Contact corrosion

[a]See Tables 1-5 for experimental details.
[b]PEG from electrolyte entered the film.

conductor and the lead to the external circuit. Although the appearance of bleaching could also be given by mechanical loss of the dye from its outer surface next to the solution, there was no direct evidence of this. The probable mechanisms (a), (b), and (c) apply to long-term cycling; they are not suggested to account for the color decrease or translucency that commonly occurs in the first few cycles.

The bleaching mechanism was recognizable as gradual decreases in q, A_G, and A_R throughout the cycling process. The loss of adhesion, with consequent increase of resistance, also tended to be gradual and was evident in a smaller switching charge without a major drop in absorbance. Corrosion of the electronic contact occurred abruptly (on the logarithmic time scale) in long-term experiments as the electrolyte penetrated the epoxy insulation on the upper portion of the electrode. A rather striking indication of this condition was the climbing q vs t curve illustrated by Fig. 4(C). A non-reversing electrochemical background process was then superimposed on the electrochromic response. The corrosion also was confirmed by visual inspection of the contacts after disassembly of the cells. Contact corrosion is an artifact of these experiments--not a basic limitation of the electrochromic system. This problem should be correctible with improved sealing of the contact. The orange/green or orange/blue-green cycling characteristics of the various types of cells are discussed further in Parts 3-6 below. The results of orange/blue cycling are discussed in Part 7.

3. Electrodes in KCl and KCl-HCl Electrolytes. Different Substrates and Cycling Routines

Cycling data for KCl and KCl-HCl electrolytes are given in Tables 1 and 2. Table 1 also includes results with different conductive substrates. Charge and absorbance plots representative of these systems are shown in Figures 7-9. For the neutral KCl electrolyte, Figures 7 and 8, the principal failure mode appeared to be bleaching, whether the substrate was SnO_2/glass, ITO/glass, or ITO/polyester. This is suggested by the systematic decreases in q and A_G, and some drop in A_R, with continued cycling. The life of about 5×10^4 cycles is comparable to those reported previously for lutetium diphthalocyanine films in neutral aqueous chloride, bromide, or fluoride electrolytes.[11,13]

Although some investigators attributed such a bleaching effect to the presence of hydroxide ion,[13] it is difficult to envision significant concentrations of that ion present in KCl at potentials between +0.95 V and -0.20 V vs Ag/AgCl. A more probable bleaching agent would seem to be an active oxygen or chlorine species formed during the anodic pulse. Possible remedies for the bleaching problem include (a) variation of the cycling routine, (b) use of acidic electrolytes to decrease oxygen formation, (c) use of nonaqueous electrolytes, and (d) measures that accelerate the dye reaction kinetics so that the display user will not tend to overdrive the electrode.

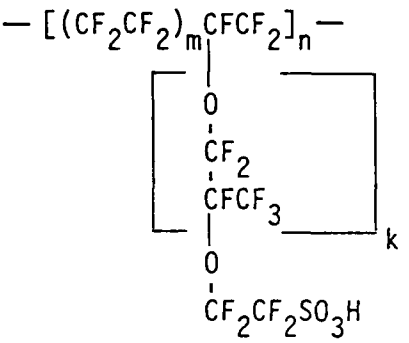
Figure 8 and Table 2 give results on 4-level cycling in 1M KCl. This drive technique is designed to minimize background reactions such as oxygen formation by holding the electrode at null potentials most of the time.[1] The scope of the present project did not include a full evaluation of the 4-level driving method, but its usefulness had been demonstrated in prior Rockwell studies. It is clear from comparison of Figures 8(B) and 8(D) that the dye film of Electrode 13 was less faded after 10^6 cycles on the 4-level routine than that of Electrode 1 at 10^6 cycles on 2-level cycling. Four-level voltage pulsing and similar drive methods merit further investigation.

Addition of 0.033M HCl to the 1M KCl electrolyte lowered the pH from 7 to 1.8 and increased the cycle life approximately 10-fold, according to the results on Electrode 5. The corresponding charge and absorbance plots are shown in Figure 9. The values of A_G and A_R remained essentially constant until the final abrupt decrease in q occurred near 5×10^6 cycles. At that point, the film remained in the green state, even at +0.95 V. Some resistance may have developed earlier within the dye film, as indicated by the sloping q curve, but the ultimate cause of failure probably was corrosion of the tin oxide/silver contact. Results on other acidic electrolytes are discussed in Part 6 below.

Change of the conductive substrate from SnO_2/glass to ITO/glass or ITO/polyester did not produce major changes in the cycling characteristics, although the absorbance data became somewhat scattered. Again, the major cause of failure appeared to be the bleaching action. These results are significant in that they show feasibility of substituting conductive oxide layers fabricated by sputtering or other low-temperature processes for the pyrolytic tin oxide formed at high temperatures. Eventual benefits from this information could include greater flexibility in the processing sequence and lower manufacturing cost for the display.

4. Electrodes with Nafion Binder

Nafion is a perfluorosulfonic acid polymer with the structure II



II

In an early stage of this work, the Nafion was applied by immersing the dye electrode in a water-propanol solution of the polymer, then withdrawing it and allowing the volatile solvents to evaporate. This was done with fresh lutetium diphthalocyanine films and with some that had been preconditioned by brief electrical cycling to make the film more penetrable to the binder. Dye films of both kinds that were Nafion-treated by simple immersion exhibited nonuniform switching characteristics. Some areas within a given electrode showed better cycling behavior, but the effect was difficult to reproduce. It was confirmed by Auger analysis that the polymer had penetrated the dye layer.

Subsequently, the improved method of Martin et al. for fabricating thin films of Nafion became available.[7] That procedure, which uses a higher-boiling solvent, was described in Section II-C-1. Much better results, recorded in Table 3, were obtained in this way. The orange/green switching was uniform over the dye area, and the cycle life was improved, approximately one order of magnitude with the SnO_2/glass substrate in 1M KCl and two orders of magnitude with ITO/glass. The results with ITO/polyester and Nafion were less definitive but appeared to follow the same trend. Plots of cycling data for Electrodes 15, 18, and 23, with the Nafion binder, are given in Figures 10 and 11.

Nafion adhered strongly to the dye and apparently offered some protection from the bleaching action. Failure of the electrodes was accompanied by visible peeling of the composite, flexible Nafion/dye film from the substrate. This probably resulted from swelling due to hydration of the polymer. In its final condition, the dye tended to remain red, as indicated by the absorbance plots in Figures 10(B) and 11(B). With some nonaqueous solvents or with changes in the electrode fabrication procedure, Nafion could prove to be a very useful component in the electrochromic cells.

5. Electrodes with PEG Plasticizers in KCl

Poly(ethylene glycol) (PEG) with a molecular weight of 300 has been used effectively as a plasticizer to increase the mobilities of ions in organic solid electrolytes.[14,15] Since electrochromic switching in the diphthalocyanine film depends on mobile counter ions, it was expected that the same type of plasticizer might increase the switching speed. That it could extend the cycle life also appeared possible if the additive retarded aggregation or crystallization of the dye.

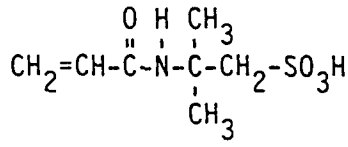
Poly(ethylene glycols) of molecular weights 300 and 3350 were introduced by incorporating them in the 1M KCl electrolyte. Table 4 gives the corresponding cycle-life data, and Figure 12 provides an example of the charge and absorbance plots.

Electrodes 24-27, with PEG (300) in KCl, may be compared with Electrodes 1-4 in KCl only. There was some overlap in the cycle-life values, but no major improvement could be attributed to the glycol. The decrease in charge with cycling was similar, although the additive appeared to retard the bleaching action to some extent. It also hindered switching, so that the film reached a mixed orange-green condition near 10^6 cycles.

In the case of PEG (3350), the polyglycol was clearly detrimental; only ~ 1000 cycles were attained with 0.1% or 1% PEG in the solution. Although the PEG interacted with the dye material, it apparently interrupted the electronic contacts between regions of dye or between the dye and the tin oxide. On the basis of this limited plasticizer investigation, other approaches to electrode improvement are preferred.

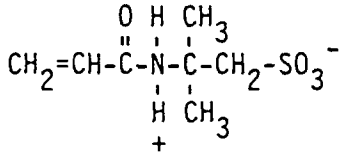
6. Electrodes in KCl-AMPS and KCl-PolyAMPS Electrolytes

Results were much more positive with the AMPS-type additives, which also were introduced through the solution phase. The structure of AMPS (2-acrylamido-2-methylpropanesulfonic acid) is



III

In the sodium salt form, the hydrogen of the $-SO_3H$ group is replaced by sodium, and ionization to $-SO_3^-$ and Na^+ is essentially complete. In contrast, the acidic compound exists partially as the dipolar ion, or internal salt IV.



IV

It was conjectured that the dipolar character could enable the AMPS to complex with the dye in any of its ionic oxidation states, resulting in bulky structures that would not readily form crystals. Lutetium diphthalocyanine electrodes in contact with polyAMPS had been investigated briefly by Sammells and Pujare.[16] In that case, the polymer was applied over the dye as a thin layer containing aqueous KCl or K_2SO_4, which was then allowed to dry. Cyclic voltammograms on those electrodes correlated with cyclable color changes, the full range from orange to violet being found only with the chloride mixture. Long-term cycling experiments were not included in that study.

Further basic research is needed to determine the mechanism of AMPS-dye interactions, with or without water, but the cycling behavior was found in the present work to be strongly and favorably influenced by the additive.

Table 5 gives the results of cycling lutetium diphthalocyanine electrodes in 1M KCl containing AMPS, NaAMPS, or polyAMPS. The dependences of charge and absorbances on total cycles is shown for some of the acidic electrolytes in Figures 13 and 14, while those for the neutral NaAMPS solution are found in Figure 15. At pH 0.59-1.5, the cycle life based on charge was consistently in the millions of cycles. This is two orders of magnitude greater than the life in 1M KCl alone. In contrast, the neutral NaAMPS electrolyte gave cycling characteristics not very different from those in KCl. This is evident on comparison of Electrodes 1 and 39; the q curves were similar, but the color separation was less pronounced with NaAMPS present.

The effectiveness of acidic AMPS-type materials is consistent with uptake of the additive by the dye film and cannot be explained by acidity alone. For example, comparing Electrode 37 in KCl-polyAMPS at pH 1.5 with Electrode 5 in KCl-HCl at pH 1.8, (Figures 14 and 9) one finds that the cycle life was ten times greater with the polyAMPS present.

The polymeric form of AMPS may be preferable to the monomer in yielding a somewhat longer cycle life, but additional data would be required to confirm this point. The absorbance plots in Figure 14 suggest that a break-in period, consisting of about 200 cycles, may have been required to open up the dye structure when the polymer was present. This effect was not observed with the acidic AMPS monomer.

The electrode-failure characteristics in the AMPS and polyAMPS cells were quite distinctive, as indicated by Figures 13 and 14. The AMPS cells showed essentially constant values of A_G and A_R, and relatively constant q, until the charge dropped abruptly beyond 10^6 cycles. As noted in discussion of the KCl-HCl cell in Part 3, this type of failure was due to corrosion of the electronic contact. The absence of bleaching in the AMPS, polyAMPS, and HCl cells suggests that an elemental oxygen species, rather than chlorine, caused the color fading in the neutral KCl electrolyte.

One caution should be observed in long-term uses of AMPS type additives. The acrylamidosulfonic acid undergoes gradual hydrolysis, especially at elevated temperatures.[17] Further work is needed to assess the possible influence of this process

on the electrode performance, although preliminary experiments with the known decomposition products, reported in Part 9 below, did not reveal any major effects. In any event, it is probable that more stable organic compounds related to AMPS also would be effective in extending the cycle life.

In one cell, containing 0.25M polyAMPS, the usual silver paste contact to the tin oxide was replaced by gold. The results, for Electrode 38, are shown in Figure 15. Good performance was observed, with a life of 1.2×10^6 cycles based on charge, but this life did not exceed that in some of the other polyAMPS or AMPS cells.

7. Orange/Blue Cycling

The results of cycling into the blue region with air carefully excluded are given in Table 6 and Figure 16. Because the cells remained in the glove box during these measurements, the colors of the films were monitored only by visual observation. The negative pulse levels were set, in accordance with the pH, to switch the dye somewhat beyond the blue-green (light blue) state, which is the 1-electron reduction product of the green.[4] Complete switching to the dark blue or violet tends to cause more damage to the film and was avoided for that reason in this limited study.

The shorter cycle life, on the order of 5×10^4 cycles, is consistent with that reported by other investigators for the orange/blue transition.[18] The plots of q vs t in Figure 4 show no major differences for cells with KCl and HCl electrolytes. The 0.25M AMPS additive may have had some deleterious effect on Electrode 43, but a firm conclusion on this point should not be drawn from one experiment. Contact corrosion may have occurred, for example.

Visually, the major cause of electrode failure in orange/blue cycling was seen to be cracking of the dye film and/or peeling of the film from the tin oxide substrate. This probably was due to formation of gaseous hydrogen during the cathodic pulse. A 4-level pulsing routine should offer at least a partial solution to this problem, since it greatly decreases the opportunity for such background reactions to take place.

An interesting change occurred on removal of the cycled cells from the glove box after they had virtually stopped switching. As traces of air leaked into the cells, some of the electrodes recovered part of their switching capacity. Similar effects related to oxygen had been observed on previous occasions in this laboratory. Further

investigations on the role of oxygen[10] or other electron acceptors in this system could lead to major increases in the cycle life for switching into the blue and violet color ranges.

8. Surfactant and Silane Treatments

Previous research in this laboratory had shown that direct chemical reactions of a lutetium diphthalocyanine film with solutions of oxidizing agents could be accelerated by pretreating the film with a surfactant.[8] This caused the film to become more porous and therefore more easily penetrated by the reactive species. From those results, it appeared possible that surfactant treatment could accelerate the electrochemical switching by the same mechanism. However, the dye electrodes treated with Witcamine AL 42-12 were actually found to be unswitchable under voltage pulsing. Apparently the dye-tin oxide contact was disrupted by the surfactant in that case. With appropriate modification, such an approach might succeed, but it was not pursued further in this project.

Silanes have been used extensively to couple reactive groups to electrode surfaces through oxygen-silicon linkages.[19] The possibility of promoting adhesion of the dye to the tin oxide in this way was investigated briefly, as described in Section II-C-3. It was found that the dye films prepared on silane-treated tin oxide were switchable under the usual voltage pulsing routine, but they showed no obvious improvement over those deposited on bare tin oxide. The silanized electrodes were not subjected to long-term cycling.

9. Cyclic Voltammetry and Dye-Film Resistances

Cyclic voltammetry was used essentially as a screening method to characterize the behavior of fresh dye electrodes in various electrolytes. It is not equivalent to an accelerated aging test, however, since long-term effects will not always be predictable from early-stage voltammograms.

Examples of the current-voltage curves for lutetium diphthalocyanine are shown in Figure 17. Long cycle life is more likely to be found with systems in which the voltammograms have low background currents and sharp, well defined pairs of current peaks with the forward and reverse processes occurring near the same voltage. When

Visually observed colors: B(dark blue), BG (blue-green), G (green), O (orange), P (purple)

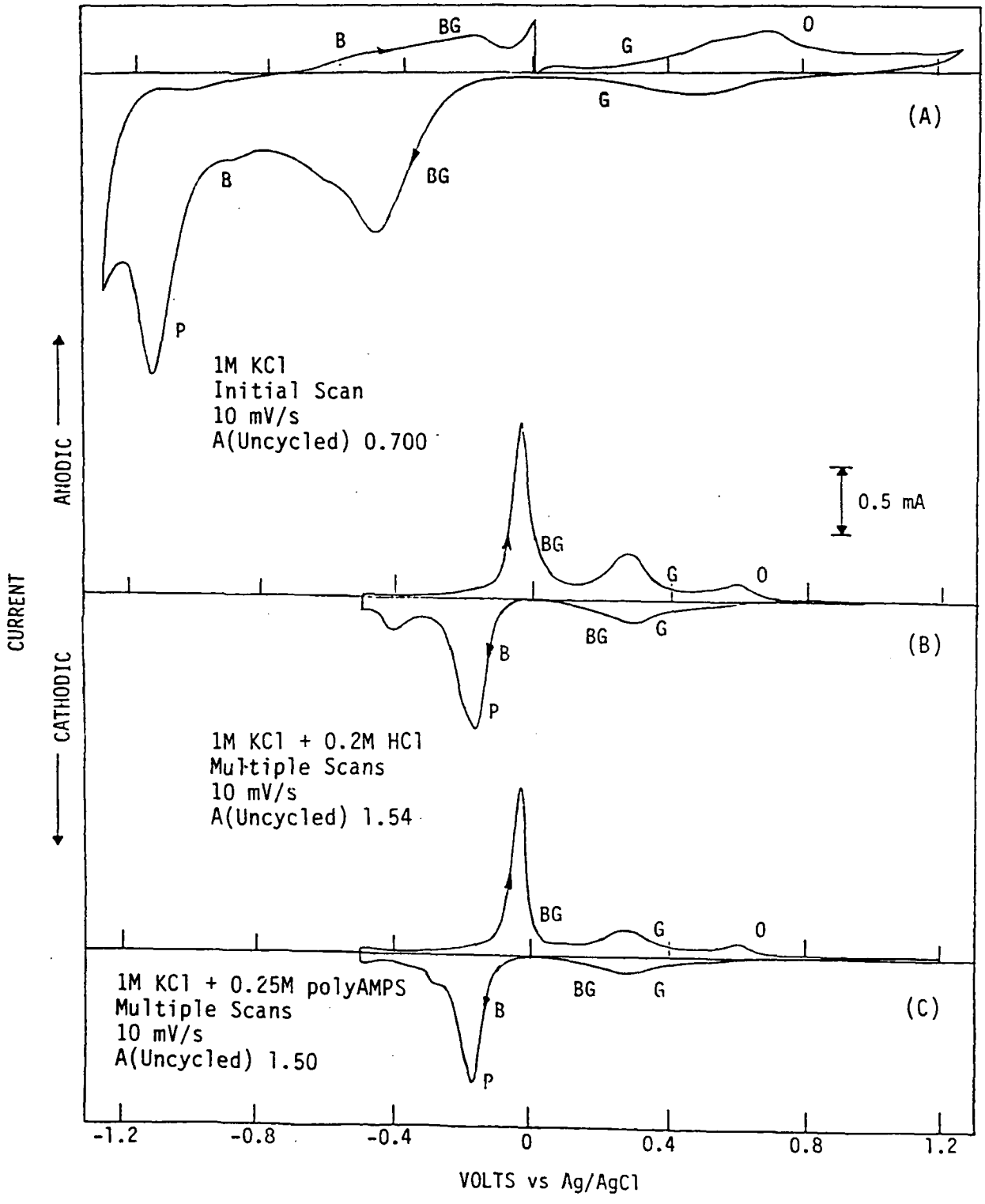
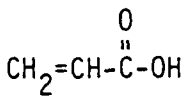


Figure 17. Cyclic Voltammograms for Lutetium Diphthalocyanine Electrodes in Aqueous Chloride Electrolytes

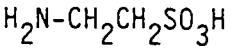
these conditions prevail, there will be less tendency to overdrive the cell in order to get fast color responses. Overdriving should to be avoided because it can decompose the electrolyte, forming products that dislodge the film or bleach it chemically.

Curve (A) in Figure 17 represents the relatively short-cycle-life dye/KCl system, while Curves (B) and (C) represent long-life systems containing HCl and polyAMPS, respectively. Compression of the color changes to a narrower voltage range in (B) and (C) is very consistent with results from our previous color study made near zero-current conditions.[4]

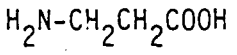
Other additives examined by cyclic voltammetry in the presence of 1M KCl included HCl, acrylic acid (V), taurine (VI), β-alanine (VII), and sulfanilic acid (VIII).



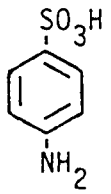
V



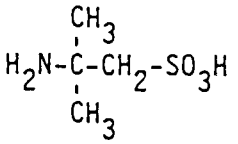
VI



VII



VIII



IX

Acrylic acid is formed by hydrolysis of AMPS, and taurine is closely related to β,β-dimethyltaurine (IX), the other hydrolysis product. Beta-alanine and sulfanilic acid were of interest because they can form dipolar ions.

Selected criteria for electrode improvement, based on voltammetric peak potentials for the color transitions, are as follows:

O/G	Average of peak potentials closer to reversible value of 0.55V
	Smaller separation between anodic and cathodic peaks
G/BG*	Smaller peak separation
BG/P**	Smaller peak separation
	Greater separation of cathodic peak from hydrogen evolution potential of electrolyte

Electrolyte additives for which the voltammograms would predict improved dye-electrode performance, relative to that in 1M KCl alone, are indicated in Table 8 with a plus sign. Those showing definite adverse effects are noted with a minus sign. All of the acidic solutions produced some beneficial effects, AMPS being preferred over HCl according to these limited observations.

Voltammograms (not shown) were also recorded for lutetium diphthalocyanine films in nonaqueous propylene glycol containing 1M KCl. Interest in glycol electrolytes for the electrochromic displays had begun with the work of Collins and Schiffrin, who reported lifetimes of several million cycles for the red/green transition of rare-earth diphthalocyanine films in ethylene glycol solutions of chloride and fluoride salts.[20] Unfortunately, the reduced blue and purple forms of the dye material are soluble in both ethylene and propylene glycols. With a Nafion coating, however, the full range of colors could be observed, the pair of blue/purple transition peaks occurring at -0.98 and -1.16 V vs Ag/AgCl. Thus, further experimentation on the use of Nafion to retard dissolution in glycol-based electrolytes would be of interest.

In related experiments, we examined the effect of propylene glycol vapor on the resistance of a lutetium diphthalocyanine film in the green and orange color states on a sapphire substrate. Nafion was not present. The orange form was produced in situ by

*Also called light blue.
**Sometimes called dark purple-blue.

TABLE 8

EFFECTS OF ELECTROLYTE ADDITIVES ON CYCLIC VOLTAMMOGRAMS OF LUTETIUM DIPHTHALOCYANINE IN 1M KCl[a]

Additive			Color Transition		
Compound	Conc (moles/l)	pH	O/G	G/BG	BG/P
AMPS	0.24	0.7	+	+	+
HCl	0.033	1.5	+	+	+
Sulfanilic Acid	0.052	2.3	+	+	
Taurine	0.25	5.4		+	-
β-Alanine	0.25	7.1	+		-

[a]A plus sign indicates improved electrode behavior, and a minus sign, poor behavior; in other cases, the results were inconclusive, or the voltammograms were not well defined.

brief exposure of the film to chlorine gas. Hence it could be represented in the simplest case as $LuPc_2^+Cl^-$. The film resistances measured at 1000 hz are given in Table 9. Most of the increased conduction in the chlorine-treated film probably was electronic, due to mixed oxidation states of the dye, i. e., to traces of green within the red layer, although the chloride ion also is known to be mobile. The glycol vapor caused only a slight resistance decrease in each case and apparently had no major plasticizing effect on the oxidized form of the dye.

10. Color Improvement

Lutetium diphthalocyanine provides colors in the green, blue, and purple or violet ranges that are acceptable to most observers. The color of the 1-electron oxidized material is orange. This can be blended with the green to form yellow,[4] which is a useful color. It was desired to demonstrate in this project that a red hue also can be obtained with a diphthalocyanine electrochromic material. For that purpose, neodymium diphthalocyanine was prepared and evaluated in the form of a sprayed film on tin oxide.

Colors in the neodymium system that were identified by visual matching with Munsell standards[21] are noted on the cyclic voltammogram of Figure 18. The green was absent in the 1M HCl electrolyte, but two well-defined pairs of current peaks appeared, which were associated with red-purple/blue-green (RP/BG) and blue-green/purple-blue (BG/PB) processes. The absence of a true green is normal in a strongly acidic solution. A better green probably can be attained at higher pH.[4] The red-range color, which was of primary concern, is compared with that of the lutetium diphthalocyanine system in Table 10. The observed color 7.5 RP 7/8 is visually consistent with 10 RP 6.2/7.5, which was calculated from a spectrum in the literature[22] for an oxidized film of neodymium diphthalocyanine. The 10 RP hue is definitely redder than the corresponding 3.8 YR hue that is typical of the lutetium system. Moreover, the spectrum of the red-purple film included a major transmission band at 642 nm, which is very close to that of a true red at 650 nm.

Though limited in scope, these results provide experimental confirmation that the hue of the reddish display color can be improved by changing the rare-earth ion. The Munsell value of the color is determined by the film thickness, which is easily controlled. A recommended approach for improving the chroma, or color purity, has been described to ONR in another paper.

TABLE 9
EFFECTS OF PROPYLENE GLYCOL VAPOR ON RESISTANCES OF LUTETIUM DIPHTHALOCYANINE FILM

Color State	Film Resistance (Ohms)[a]	
	Dry N_2	N_2 + PG
Green	1.72×10^7	1.33×10^7
Orange	7.86×10^5	6.66×10^5

[a]AC current-voltage measurement at 1000 Hz.

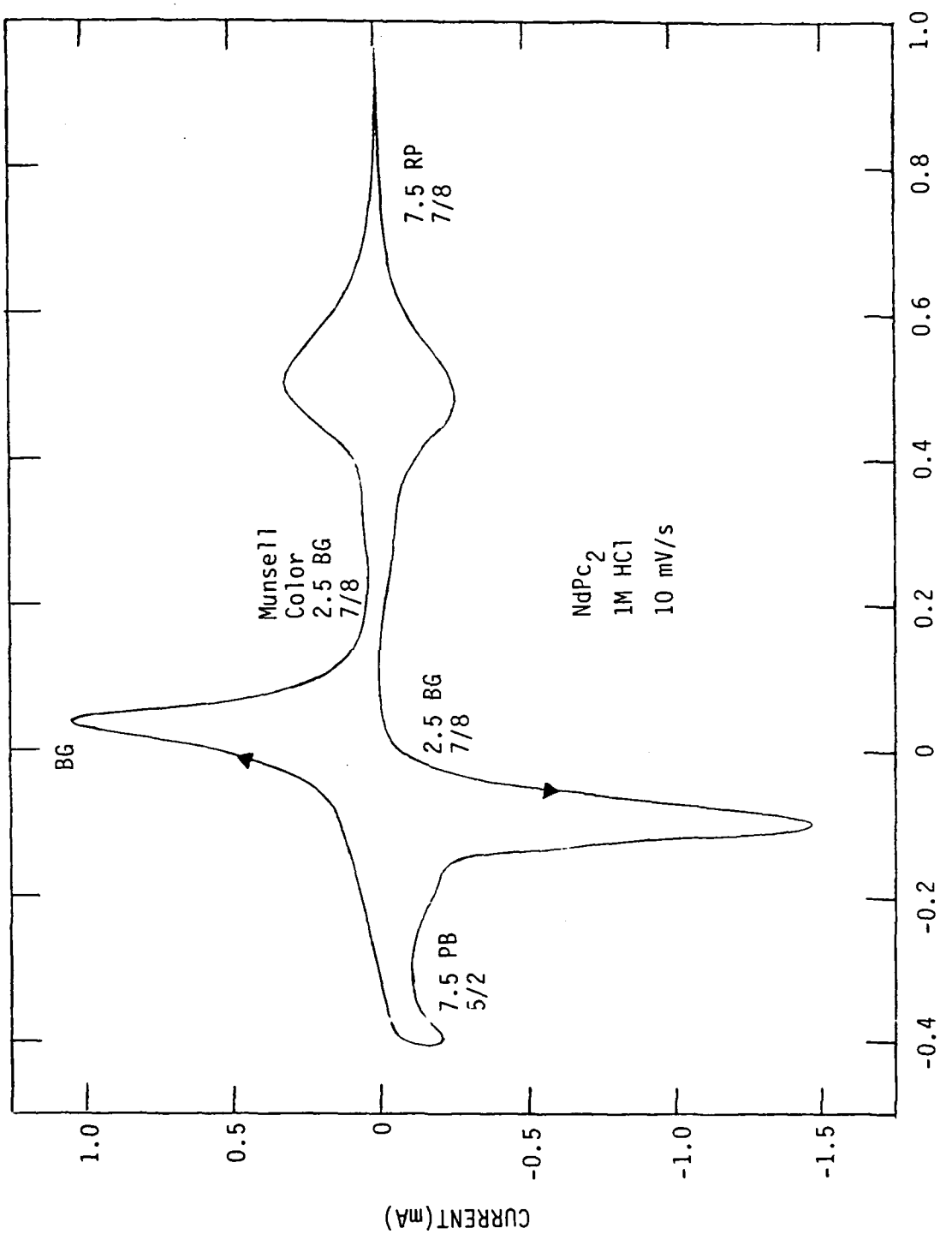


Figure 18. Cyclic Voltammogram of Neodymium Diphthalocyanine Electrode in 1M Hydrochloric Acid

TABLE 10

COMPARISON OF RED-RANGE COLORS IN OXIDIZED RARE-EARTH DIPHTHALOCYANINE FILMS

Rare Earth	Ref.	Electrolyte	Munsell Notation		CIE Notation			Appearance
			Hue	Value/Chroma	Y	x	y	
Lu[a]	4	1M KCl	3.8 YR	6.8/5.2	40.3	0.40	0.36	Orange
Nd[a]	22	5M $NaClO_4$	10 RP	6.2/7.5	32.0	0.39	0.31	Plum
Nd[b]	This study	1M HCl	7.5 RP	7/8	42.9	0.42	0.34	Mauve

[a]Calculated from spectrum of oxidized film, adjusted to A_{665} = 2.00 in green state.
[b]Visual match with Munsell standard color.

B. COUNTER ELECTRODES

Results of controlled-current cycling of silver-silver chloride and lead-lead fluoride counter electrodes are summarized in Tables 11 and 12, respectively. Figure 19 shows representative potential-time plots for Ag/AgCl in 1M KCl taken from oscilloscope traces with square-wave and sawtooth input currents.

The small voltage shifts for Ag/AgCl, measured with respect to a similar electrode at zero current, are consistent with the reliable behavior of this system in many long-term cycling experiments on lutetium diphthalocyanine cells. The vertical portions of the square-wave traces were mostly due to ohmic drop in the electrolyte. Although Ag/AgCl may not be the ultimate counter-electrode choice in the electrochromic displays, it does not present a problem at this stage of the device development, except for the fact that it requires a chloride electrolyte to function properly.

The behavior of Pb/PbF_2 in 1M KF was not quite as satisfactory, but this system was not prepared in a highly porous, strongly adherent form, as was the Ag/AgCl. If a comparable fabrication process were developed for the Pb/PbF_2 electrode, it probably would perform as well as Ag/AgCl, eliminating the restriction of a chloride-containing electrolyte and any possible problem associated with anodic oxidation of chloride ion.

Polyvinylferrocene[23] was identified as a candidate material for a very different type of counter electrode, which would not require the presence of a specific cation or anion in the solution. There was not sufficient time to evaluate this organic counter electrode system in the laboratory. It is noted here as an interesting alternative to the metal/insoluble-salt type represented by Ag/AgCl and Pb/PbF_2.

TABLE 11

POTENTIAL SHIFTS IN CONTROLLED-CURRENT CYCLING OF Ag/AgCl ELECTRODES IN 1M KCl

A. SQUARE-WAVE CURRENT[a]

Electrode Area (cm^2)	Initial Charge Density (C/cm^2)	Current Density (mA/cm^2)	Cycles	Potential Shifts (Volts) Anodic	Cathodic
0.16	5.0	6.4	3.00×10^3	0.020	-0.032
			8.66×10^5	0.021	-0.031
0.16	6.1	6.4	2.40×10^3	0.012	-0.021
			8.64×10^5	0.014	-0.021
0.16	6.1	6.4	3.90×10^3	0.021	-0.032
			8.78×10^5	0.022	-0.036
0.19	1.6	5.3	3.60×10^3	0.025	-0.023
			8.78×10^5	0.025	-0.036

[a]Cycling Routine: 0.1 s at 1 mA and 0.1 s at -1 mA.

B. SAWTOOTH CURRENT[b]

Electrode Area (cm^2)	Maximum Current Density (mA/cm^2)	Cycles	Potential Shifts (Volts) Anodic	Cathodic
0.16	13	5.62×10^3	0.042	-0.056
		1.58×10^6	0.042	-0.056
0.16	13	4.50×10^3	0.040	-0.072
		1.58×10^6	0.042	-0.056
0.16	13	2.62×10^3	0.034	-0.052
		1.58×10^6	0.036	-0.046
0.19	11	0.75×10^3	0.048	-0.074
		1.58×10^6	0.052	-0.054

[b]Cycling Routine: Period 0.16 s; peak current ± 2 mA.

TABLE 12

POTENTIAL SHIFTS IN CONTROLLED-CURRENT CYCLING OF Pb/PbF_2 ELECTRODES IN 1M KF

A. SQUARE-WAVE CURRENT[a]

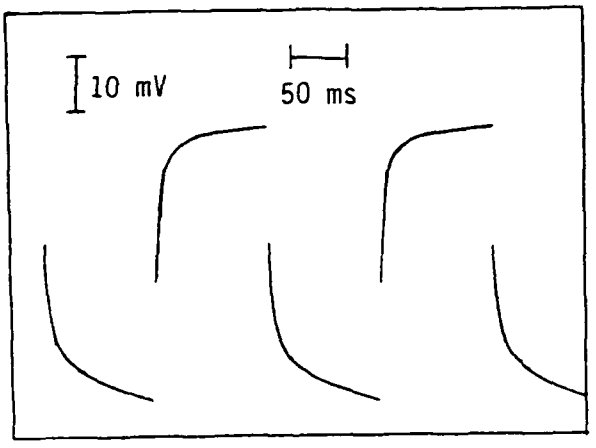
Electrode Area (cm^2)	Initial Charge Density (C/cm^2)	Current Density (mA/cm^2)	Cycles	Potential Shifts (Volts) Anodic	Cathodic
0.11	5.4	9.1	1.20×10^3	0.030	-0.15
			4.71×10^5	0.035	-0.17
0.10	10	10	0.90×10^3	0.034	-0.08
			4.72×10^5	0.034	-0.10

[a]Cycling Routine: 0.1 s at 1 mA and 0.1 s at -1 mA.

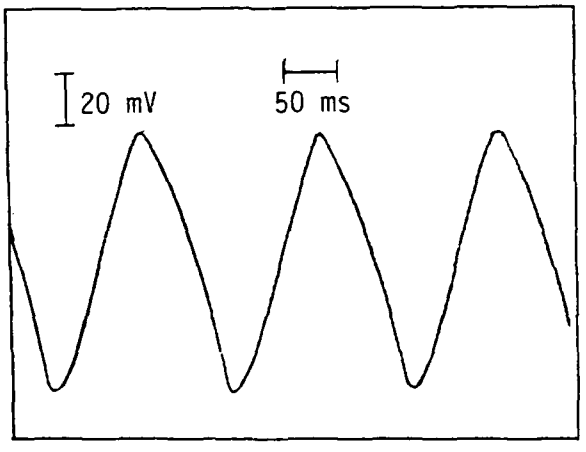
B. SAWTOOTH CURRENT[b]

Electrode Area (cm^2)	Maximum Current Density (mA/cm^2)	Cycles	Potential Shifts (Volts) Anodic	Cathodic
0.10	21	~ 0	0.17	-0.14
		1.01×10^6	0.15	-0.32

[b]Cycling Routine: Period 0.16 s; peak current ± 2 mA.



A. Square-Wave Input Current



B. Sawtooth Input Current

Figure 19. Potential-Time Curves for Ag/AgCl Electrode in Controlled-Current Cycling

C. CONCLUSIONS FROM EXPERIMENTAL INVESTIGATION

Conclusions from this experimental investigation are summarized below. All electrolytes used with the display electrodes contained excess chloride ion.

1. Switching charge and steady-state dye-film spectra are both useful in the evaluation of cycle life. Charge is preferred, however, as a criterion of switching capability.

2. Three failure modes are identifiable for lutetium diphthalocyanine electrodes in orange/green or orange/blue-green cycling:

(a) Bleaching, probably by chemical action, which is typical in neutral chloride electrolytes.

(b) Gradual loss of adhesion between the dye and the conductive substrate, as with Nafion-treated films, or between regions within the dye, as with some nonconductive plasticizers.

(c) Corrosion of the electronic contact between the transparent conductor and the external circuit. This corrosion, which led to a major resistance increase after many cycles, was observed in acidic electrolytes. It was due to inadequate isolation of the contact from the solution and is not a characteristic of the electrochromic system.

3. In addition to pyrolytic SnO_2/glass, a sputtered ITO/glass and a proprietary commercial ITO/polyester are usable as transparent conductive substrates for the dye film.

4. It was confirmed that the orange/green or orange/blue-green cycle life, in the absence of special additives, is longer in acidic media than in neutral electrolytes.

5. A Nafion binder adheres strongly to the dye and can increase the orange/green cycle life significantly, although swelling of the polymer eventually causes the composite film to peel away from the conductive substrate.

6. AMPS and polyAMPS, introduced as electrolyte additives, cause major increases in the orange/blue-green cycle life. Failure after several million cycles was due to corrosion of the electronic contact.

7. The failure mode in orange/blue cycling is associated with hydrogen formation in the case of aqueous electrolytes. Further research is needed to extend the orange/blue life beyond 5×10^4 cycles. Use of nonaqueous media is a promising approach, but improved electrolyte formulations are needed to prevent dissolution of the blue and purple forms of the dye. This problem has not been extensively researched.

8. The concept of improving the hue of the red display color by using neodymium diphthalocyanine instead of lutetium has been verified.

9. Silver-silver chloride is a very dependable counter electrode in electrolytes containing chloride ion. Lead-lead fluoride responds favorably in a fluoride solution but has not been as thoroughly evaluated as Ag/AgCl.

10. It is fully expected that additional research and development work on the diphthalocyanine electrochromics can lead to practical displays. The principal tasks remaining are cycle-life extension, with emphasis on the blue and purple color ranges, some further color enhancement, and adaptation of active-matrix addressing technology to the electrochromic system.

IV. FLAT-PANEL DISPLAY TECHNOLOGY ASSESSMENT

This section discusses flat-panel displays for military aircraft and large-screen uses in relation to the results of this project. For aircraft, the multicolor electrochromic is compared with plasma, light-emitting diode (LED), electroluminescent (EL), and liquid-crystal (LC) technologies in terms of use life, switching time, and power consumption. The major advantages and disadvantages of the electrochromic with respect to the other technologies are then indicated. For large screens, comparisons are made with liquid-crystal light-valve and oil-film light-valve projection displays. Literature sources examined in the preparation of this section include References 24-55.

A. AIRCRAFT FLAT-PANEL DISPLAYS

There is now major interest in flat-panel color technologies that could replace the cathode ray tube (CRT) in multifunction cockpit displays. Often present as a group of five panels,[33,47] each with a viewing area about 3 × 5 in. (7.6 × 12.7 cm), these displays present graphic symbology, advisory information, and real-time color video, including a moving map. It is desired that the five displays be interchangeable in their functions to increase flexibility and provide backup in the event of a failure. Among the usual requirements are moderate resolution (100-200 lpi) (lines per inch), wide viewing angle, high contrast, several shades of gray, full color, response time < 30 ms, wide operating temperature range (-55°C to +90°C), and use life of 2,000-10,000 hr. Reference 51 gives additional performance criteria.

Helmet-mounted displays, which now use miniature (2.54 cm diameter) CRTs, also require video capability, but in much smaller sizes and with higher resolution. The head-up display (HUD) projects the image from a small matrix panel onto a combining glass where it is superimposed on a view of the real-world scene outside the aircraft.

Although some designers would prefer to have a single display technology serve all purposes in a cockpit, it is generally expected that advanced aircraft will use more than one type. The less demanding flat-panel applications include graphic and message displays and smaller discrete displays such as clocks and multilegend switches.

Finally, it should be noted that large single-screen displays, about 1 × 1 m, will be of interest for future aircraft with encapsulated crew stations, in the event that this

concept is implemented. To save space, large directly viewed panels would be preferred to projection displays for this purpose.

The multicolor electrochromic technology actually has inherent potentialities for use in all of the above applications, but further development would be required in each case. The time and effort needed to provide an experimental prototype in a military configuration and format depends strongly on the type of display desired. For most purposes, the cycle life would need to be extended about one order of magnitude, and the gradual increase of response time with cycling would have to be prevented; the colors, especially in the red range, need optimization; in addition, active-matrix addressing[26,48] would have to be adapted for use with the electrochromic technology. All of these improvements are thought to be attainable. If detailed color specifications are excluded, the only inherent limitation foreseen is the lack of shades of gray within individual dots or segments. However, by using combinations of light and dark dots, as in offset color printing, it should be possible to achieve different depths of color. This would entail some loss of resolution.

Aircraft displays are noted below in the probable order of increasing difficulty for the electrochromic:

(a) Discrete readout with segmented characters.

(b) Discrete display in matrix form.

(c) Helmet-mounted, matrix, 500 lpi, without real-time video.

(d) Multifunction 3 × 5-in. panel, 100 lpi, full-color, real-time video.

(e) Large multipurpose matrix, 1-meter screen, 100 lpi.

Specific comparisons of the multicolor electrochromic with other flat-panel technologies competing for aircraft and large-screen displays are made in Part C of this section.

B. LARGE-SCREEN DISPLAYS

The principal Navy applications for large screens are to display information on shipboard and in land-based command centers. With more space available than in aircraft, projection displays are acceptable. Large directly viewed panels should not be ruled out in principle, although "tiling" to build a large display by edge-to-edge placement of many small panels is undesirable.

Projected images 6 × 6 ft (1.8 × 1.8 m) with a total of 4000 lines are typical of command and control needs. The resolution of the actual display, before projection, then would be 4000 lpi for a 1 × 1 in. panel, or 2000 lpi for a 2 × 2 in. This is a severe requirement; present large-screen light-valve displays for shipboard uses have about 1000 lpi before projection. Other goals for the large screens are comparable to those in aircraft flat-panel displays. Large status boards will portray graphics and characters that require only infrequent updates, but some pictorial uses could demand full-color video.

The question of high resolution needs further comment. In some electrochromic display structures, the lithography used to separate the dots could be the factor that limits the resolution of the panel. Assuming that 1-μm separation lines can be formed between the pixels, and that the total width per pixel, including one separation, is 10 μm, the resolution would be 2540 lpi. This may be attainable with the electrochromic, given its unique feature of coincident color, while 2540 pixels per inch would be very difficult with a tri-color technology using three dots for each full-color pixel.

This prospect of greatly increased resolution, with simpler structures of the display and projection equipment, provides a major incentive for developing the electrochromic as an alternative to liquid-crystal or oil-film light-valve displays. An electrochromic light-valve concept originated in conjunction with a related Rockwell Navy contract is described elsewhere. In addition to the light-valve display, a large-screen projection of an electrochromic matrix with thin-film transistor (TFT) active-matrix drive should be considered. The acceptable resolution could be considerably lower than 2000 lpi if the projection were made from a panel larger than 2 in. As with aircraft displays, large screens for status boards would be more easily achieved than large-screen video. Technology comparisons of special importance in large-screen applications are

summarized in Table 13. More detailed information on electrochromics and liquid crystals as flat-panel technologies is provided in Part C, below.

C. COMPARISONS OF FLAT-PANEL TECHNOLOGIES

In Table 14, the multicolor electrochromic system of this investigation is compared with four flat-panel display technologies that have reached a mature stage through intensive development in many laboratories. The performance data given for three important parameters--operating life, switching time, and power consumption--are representative of those in the literature, but it should be understood that all numbers in each column do not necessarily apply to one display device.

Unlike the other technologies, the electrochromic has open-circuit memory. Accordingly, the average power density at any dot or segment will be proportional to the number of times per second that it changes color. Optimized drive circuitry for an individual area of the electrochromic has not yet been designed, but this presents no unusual problems. Assumptions made for the switching frequency and drive efficiency in estimating the power consumption are indicated in footnotes to Table 14.

The multicolor electrochromic is more closely related to liquid crystals than to the three emissive displays, even though the basic mechanisms by which electrochromics and liquid crystals modulate the light are very different. The switching times are comparable, in the tens of milliseconds range (disregarding contact-resistance problems in the electrochromic, which are expected to be solved). Because the electrochromic has memory, the average power levels are estimated to be about the same for a rather fast-changing graphic display. For slower updates, such as once per minute, the electrochromic would require far less power than the liquid crystal, which has to be continuously refreshed to maintain the light-scattering state. However, power economy of the electrochromic is lost in the video mode. Not included in Table 14 is the important fact that the diphthalocyanine electrochromic has been shown to switch rapidly at a temperature as low as -50°C.[11] Liquid crystals operate in such environments only with external heating.

Advantages and disadvantages of the electrochromic with respect to each of the four flat-panel technologies are indicated qualitatively in Tables 15-18. Except for shades of gray, the inherent advantages outweigh the disadvantages, at least for some

TABLE 13

SUMMARY COMPARISON OF ELECTROCHROMIC LIGHT VALVE WITH OIL-FILM OR LIQUID-CRYSTAL[a] LIGHT-VALVE DISPLAY SYSTEMS

Advantages of Multicolor Electrochromic	Disadvantages of Multicolor Electrochromic
Coincident, multiple colors (tunable)	Color set fixed by electrochromic material
Only one projector required	Shades of gray not inherent
Higher resolution	
Simpler structure	
Easier scale-up to larger sizes	

[a]See Tables 14 and 18 for further comparisons of electrochromic and liquid-crystal flat-panel technologies.

TABLE 14

COMPARISON OF FLAT-PANEL DISPLAY TECHNOLOGIES IN TERMS OF OPERATING LIFE, SWITCHING TIME, AND POWER CONSUMPTION

Technology	Plasma	Light-Emitting Diode	Electroluminescent	Liquid Crystal	Multicolor Electrochromic[a]
Life					
Operating Time	20,000-180,000 hr	> 100,000 hr	10,000 hr	10,000-50,000 hr	> 1,700[b]
Cycles					> 3×10^6
Switching Time	20 μs	15 ns	50 μs rise	50 ms rise	25 ms[(3)]
			100 μs fall	100 ms fall	(Early cycling Stage)
Power Consumption Including Drivers					
Graphic or Status	80 mW/cm^2	640 mW/cm^2	10-40 mW/cm^2	0.3 mW/cm^2	0.9 mW/cm^2 [c]
Video Pictorial			35 mW/cm^2	0.9 mW/cm^2	50 mW/cm^2 [d]

[a]This investigation.
[b]Total time signal is applied in 3×10^6 cycles at 2 seconds per cycle; orange/green transition.
[c]Assuming average of 1.5 % of dots contrast with background and their colors change once per second with 50 % driver power efficiency.
[d]Assuming 25 % of dots change color in each 1/30 second and driver efficiency is 50 %.

applications, in all of these comparisons. It was noted in Part A of this section that deeper colors should be attainable with the electrochromic by combining light and dark dots. The darkest blue color state of lutetium diphthalocyanine is virtually blue-black.

Further work is needed to achieve full control of the colors in the diphthalocyanine systems, to increase the operating life, maintain the rapid switching characteristic of fresh films, and, for many applications, to adapt the TFT active-matrix addressing method to this type of display. To attain its goals, this technology will require significant development effort and some additional research, just as the other flat-panel technologies have required before reaching their present states of maturity.

TABLE 15

GENERAL COMPARISON OF ELECTROCHROMIC AND PLASMA TECHNOLOGIES

Advantages of Multicolor Electrochromic	Disadvantages of Multicolor Electrochromic
Much lower voltage	Slower response
Much lower power	Matrix requires TFT or other special addressing
Open-circuit memory	
Coincident color (tunable)	Requires night lighting
Higher resolution	
Can be projected	
Simpler structure	

TABLE 16

GENERAL COMPARISON OF ELECTROCHROMIC AND LIGHT-EMITTING-DIODE TECHNOLOGIES

Advantages of Multicolor Electrochromic	Disadvantages of Multicolor Electrochromic
Much lower power	Slower response
Open-circuit memory	Requires night lighting
Coincident color (tunable)	
Higher resolution	
Can be projected	
Amenable to TFT addressing	

TABLE 17

GENERAL COMPARISON OF ELECTROCHROMIC AND ELECTROLUMINESCENT TECHNOLOGIES

Advantages of Multicolor Electrochromic	Disadvantages of Multicolor Electrochromic
Much lower voltage	Slower response
Lower power (except video)	Not directly multiplexable
Open-circuit memory	Requires night lighting
Excellent viewing in high ambient light	
Coincident color (tunable)	
Higher resolution attainble	
Can be projected on screen	

TABLE 18

GENERAL COMPARISON OF ELECTROCHROMIC AND LIQUID-CRYSTAL TECHNOLOGIES

Advantages of Multicolor Electrochromic	Disadvantages of Multicolor Electrochromic
Lower voltage	Shades of gray not inherent
Open-circuit memory	Higher power in video operation
Faster response than many LC's, especially at low temperature	Not directly multiplexable[a]
Wide viewing angle	High transient currents
Requires no polarizers	
Multiple colors (tunable)	
Coincident color	
Higher resolution anticipated	
Interplate spacing not critical	
Low-temperature performance without heating[1]	
Solid-state versions feasible	

[a]Statements in the literature that active-matrix addressing is not applicable to electrochromics are incorrect. Rockwell concepts on this subject are reported elsewhere under this contract.

V. RECOMMENDATIONS

Developmental progress in device technology should be judged, not by the calendar time elapsed in its pursuit, but by the accomplishments, the benefits expected, and the total effort expended. With respect to electrochromics, it is most important to recognize that each material belongs to a unique chemical system that requires specific research and development. By far, most of the world's effort in electrochromics has been expended on the blue/white tungsten oxide system, which is now in production in Japan. Work on the multicolor diphthalocyanine technology has proceeded systematically since its inception at Rockwell approximately ten years ago.[1,2] Significant progress has been made in understanding the electrode processes, and portions of their thermodynamics and kinetics have been characterized. Through work in this laboratory and others, major developmental advances also have been made. For example, a correlation scheme relating the various colors quantitatively to pH and minimum driving voltage is available,[4] and the life has increased from a few hundred cycles in early portable demonstration units to several million cycles, a limit that is imposed temporarily by inadequate sealing of the electrode contact. An intensive advanced development effort on the diphthalocyanine electrochromics is warranted by the special capabilities of these materials, the experimental results obtained to date, and the flat-panel display requirements that are not met by any other single technology. In support of such development, some basic research also is still needed. More specific recommendations are given below.

A. RESEARCH

Near-term research should be concentrated on approaches with break-through potential. Some recommended topics, which need not be sequential or interdependent, include:

1. Color improvement by new approaches
2. Switching characteristics in the intermediate pH range of 1 to 4.
3. Electrolytes with low or zero water content.
4. Liquid or solid electrolytes compatible with blue and purple forms of the dye.

B. DEVELOPMENT

Further development effort should include:

1. Continued cycle-life studies.
2. Optimization of life, color, and speed through choice of materials and processing technology.
3. Improved sealing methods, as a comparatively small but important task.
4. Adaptation of active-matrix and/or laser addressing to the electrochromic system.

C. PROTOTYPE DISPLAYS

It is preferable to build simpler segmented or graphic models first and proceed to matrix-format displays after the addressing technology is available, at least in experimental form. It is appropriate now to begin such a drive development concurrent with further work on the electrochromic system.

D. VARIABLE OPTICAL FILTERS

Electrically variable filters are another device for which the multicolor electrochromic system clearly has potential applications. Much simpler than displays, filter models could be built and evaluated at relatively small cost. Most of the technical approaches that could advance the display technology would also improve the filters.

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